

ΜΠΣ: ΤΕΧΝΙΚΕΣ ΧΑΡΑΚΤΗΡΙΣΜΟΥ ΥΛΙΚΩΝ

ΧΕΙΜΕΡΙΝΟ ΕΞΑΜΗΝΟ 2022-2023

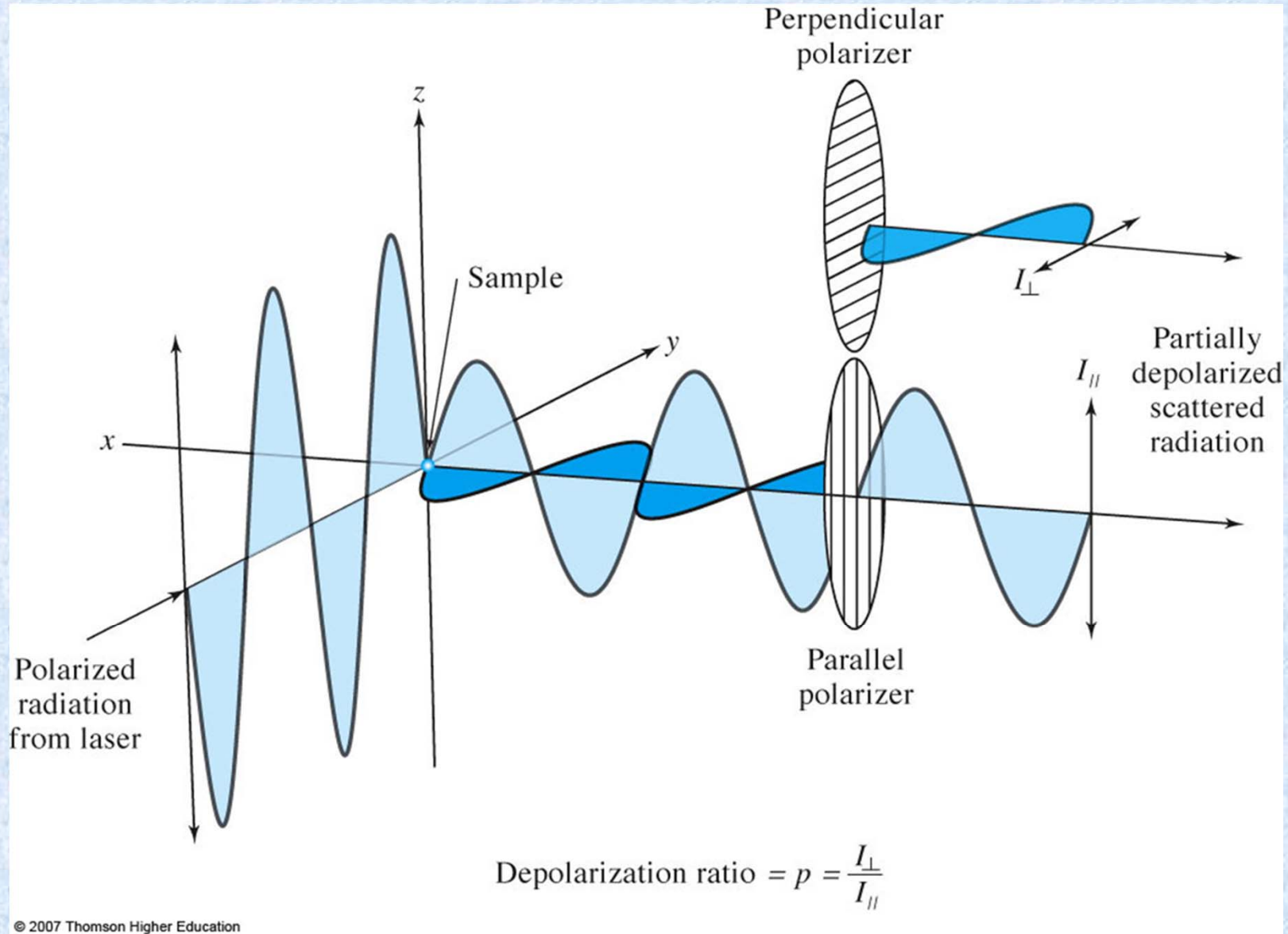
Φασματοσκοπία Raman

Β' Μέρος

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Επίσκεψη στο εργαστήριο Εφαρμοσμένης Μοριακής Φασματοσκοπίας (ΙΤΕ/ΙΕΧΜΗ)

POLARIZED RAMAN SCATTERING



DEPOLARIZATION RATIO

- The ratio of the peak intensity of the parallel and perpendicular component is known as the depolarization ratio.

$$\rho = \frac{I_{\text{perpendicular}}}{I_{\text{parallel}}} = \frac{I_{\text{depolarized}}}{I_{\text{polarized}}}$$

- The value of the depolarization ratio of a Raman band depends on the symmetry of the molecule and the normal vibrational mode, in other words, the point group of the molecule.
- Placzek's polarizability approximation:
 - the depolarization ratio of a **totally symmetric** vibrational mode is less than 0.75, and that of the other modes equals 0.75.
 - A Raman band whose depolarization ratio is less than 0.75 is called a **polarized band**, and a band with a 0.75 depolarization ratio is called a **depolarized band**.

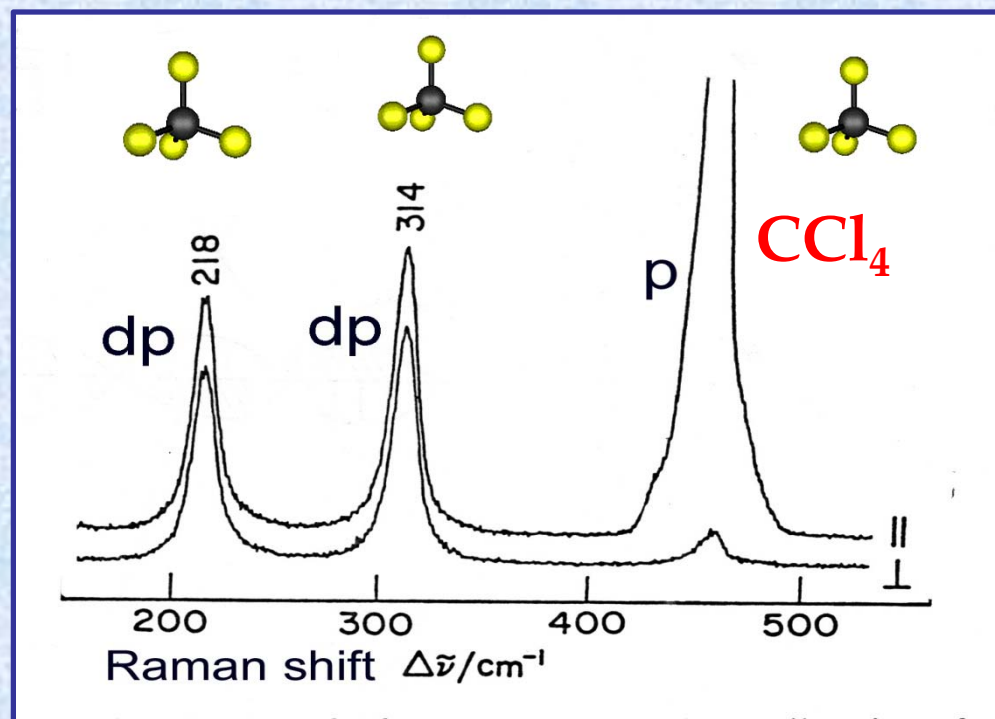
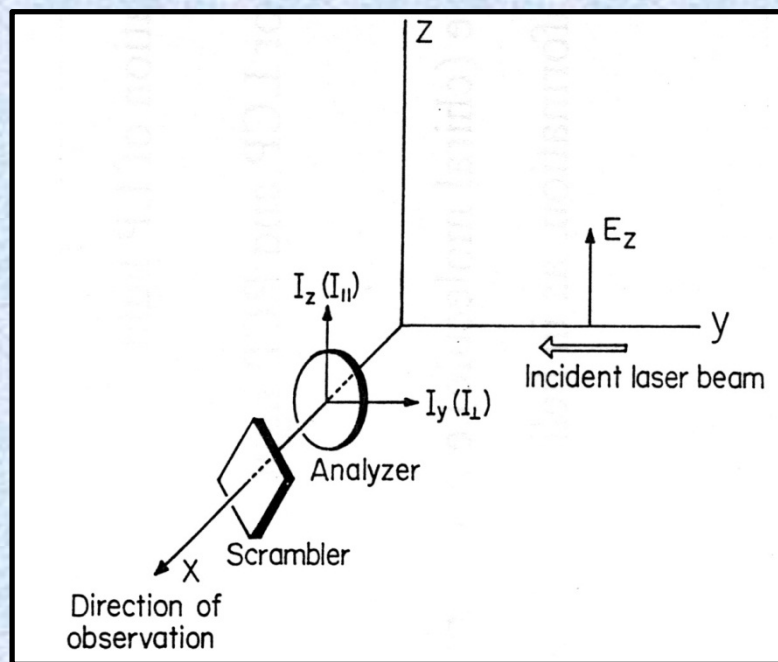
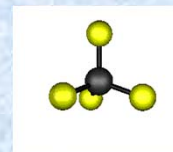
DEPOLARIZATION RATIO OF VIBRATIONAL MODES

Gives information about the **symmetry** of a vibration.

ρ_p = depolarization ratio for polarized light = $I_y/I_z = I_{\perp}/I_{\parallel}$

$0 \leq \rho_p < 0.75$: Raman line is polarized (p). Vibration is totally symmetric.

$\rho_p = 0.75$: Raman line is depolarized (dp). Vibration is not totally symmetric.



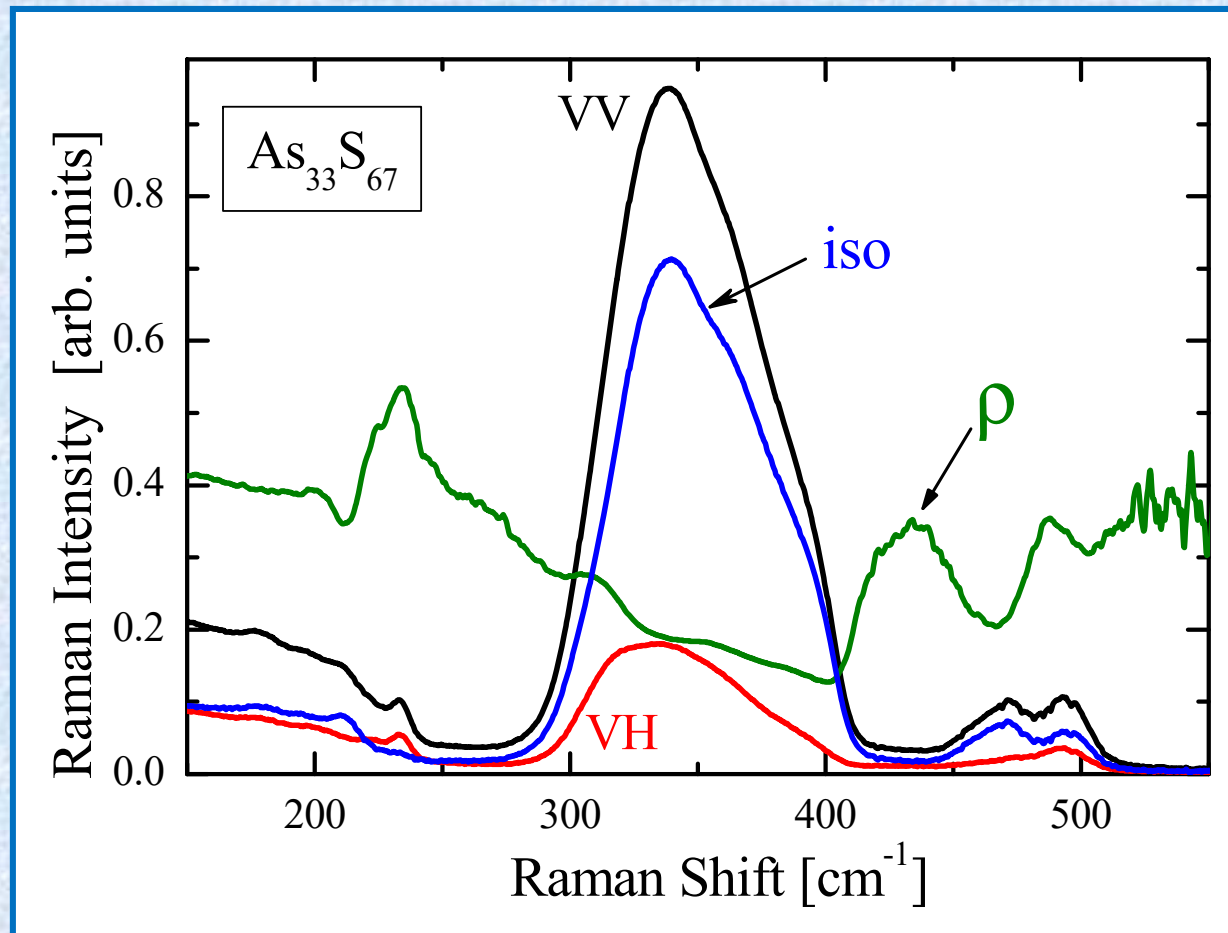
ANALYSIS OF RAMAN SPECTRA

Isotropic spectrum:
Purely vibrational component

Depolarization ratio

$$I^{iso}(\tilde{\nu}) = I^{VV}(\tilde{\nu}) - (4/3)I^{VH}(\tilde{\nu})$$

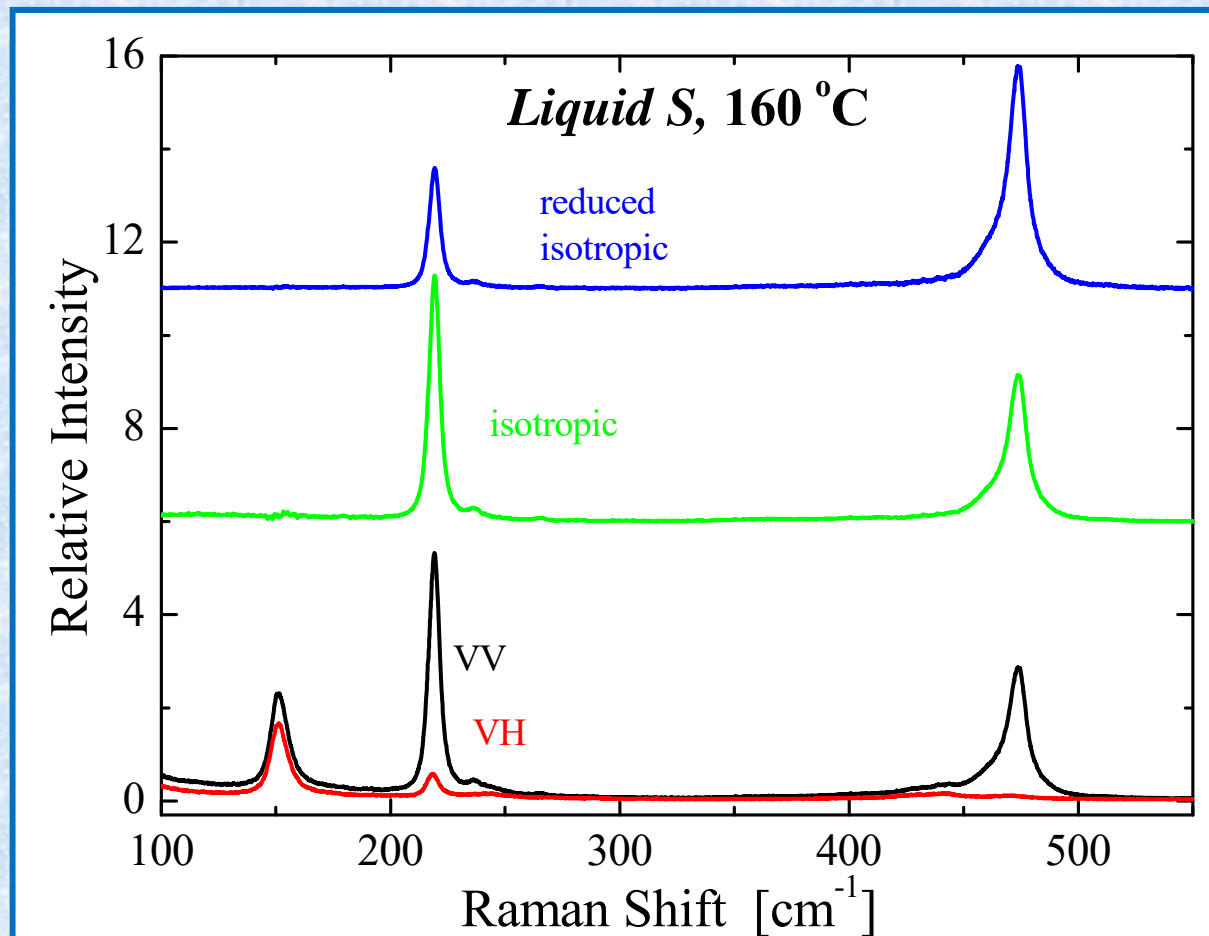
$$\rho(\tilde{\nu}) = I^{VH}(\tilde{\nu}) / I^{VV}(\tilde{\nu})$$



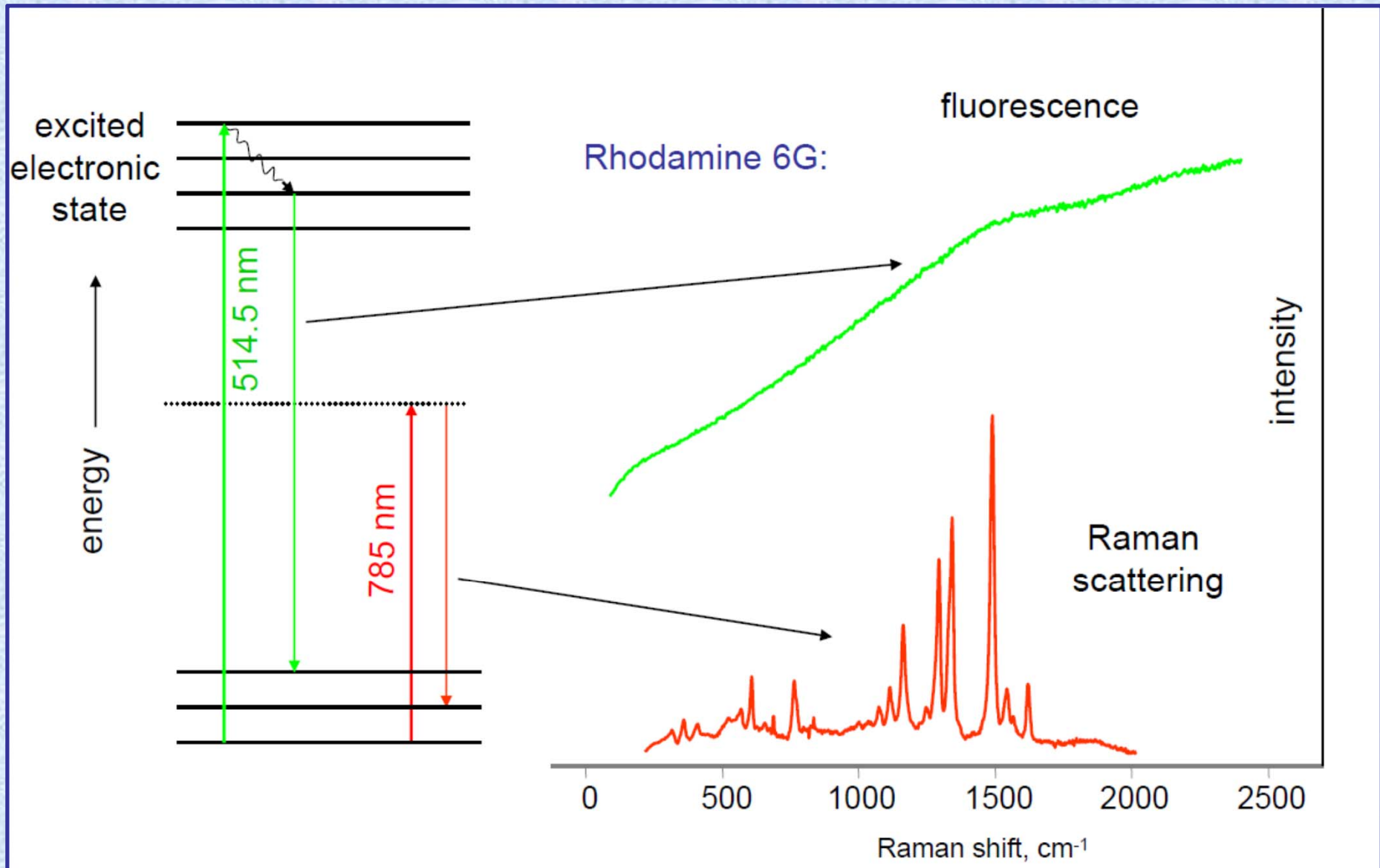
ANALYSIS OF RAMAN SPECTRA

Reduced Raman spectrum

$$I^{red}(\tilde{\nu}) = (\tilde{\nu}_0 - \tilde{\nu})^{-4} \tilde{\nu} [n(\tilde{\nu}, T) + 1]^{-1} I^{exp}(\tilde{\nu}) \quad n(\tilde{\nu}, T) = [\exp(\hbar \tilde{\nu} / k_B T) - 1]^{-1}$$

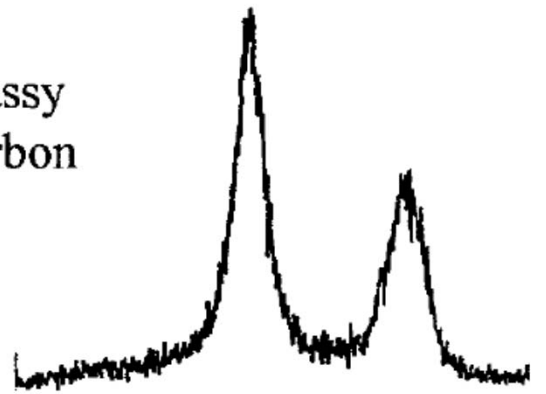


AVOIDING THE FLUORESCENCE



NOISE IMPROVEMENT

glassy
carbon



Scanning/PMT

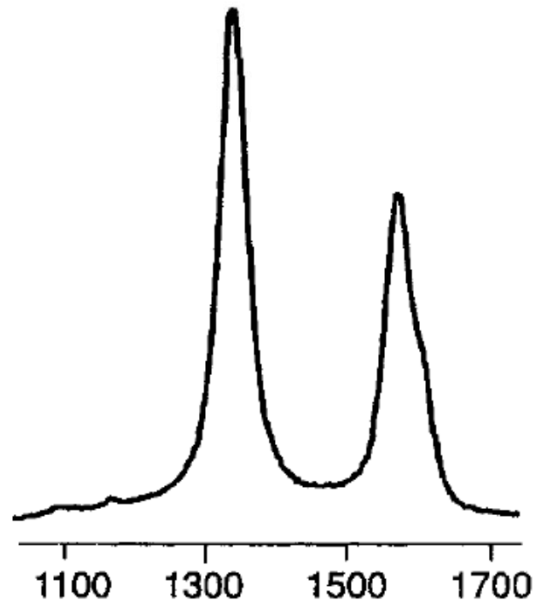
20 minutes

SNR ~ 28

CCD multichannel

5 seconds

SNR ~ 280



Raman shift, cm⁻¹

Signal-to-Noise ratio (SNR)

$$\text{SNR} = \frac{\bar{S}}{\sigma_y}$$

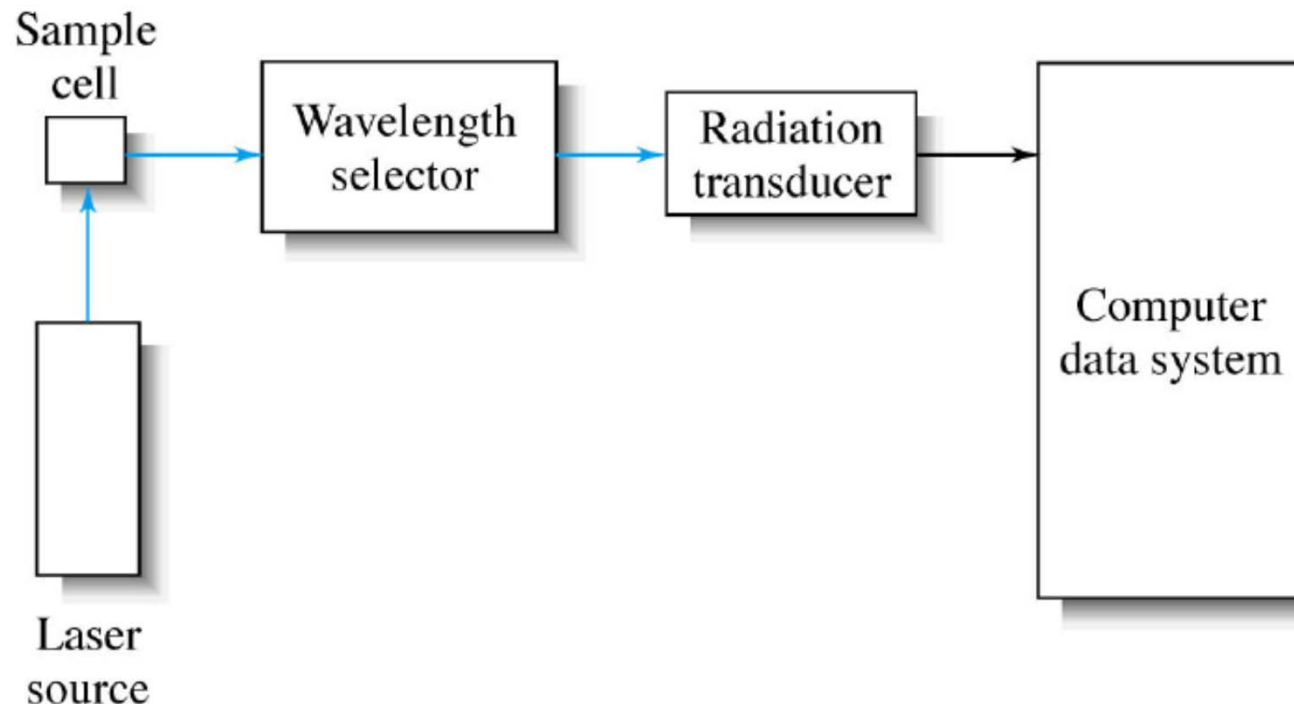
S: average peak height
 σ_y = standard deviation

$$\frac{\text{SNR}_A(\text{multichannel})}{\text{SNR}_A(\text{single channel})} = N_R^{1/2}$$

N_R : number of resolution elements

Raman Instrumentation

- Laser source
- Sample illumination system
- Spectrometer



Light Source

TABLE 18-1 Some Common Laser Sources for Raman Spectroscopy

Laser Type	Wavelength, nm
Argon ion	blue 488.0 or 514.5
Krypton ion	green 530.9 or 647.1
Helium-neon	632.8
Diode	785 or 830
Nd-YAG	1064

} **visible**

} **Near IR**

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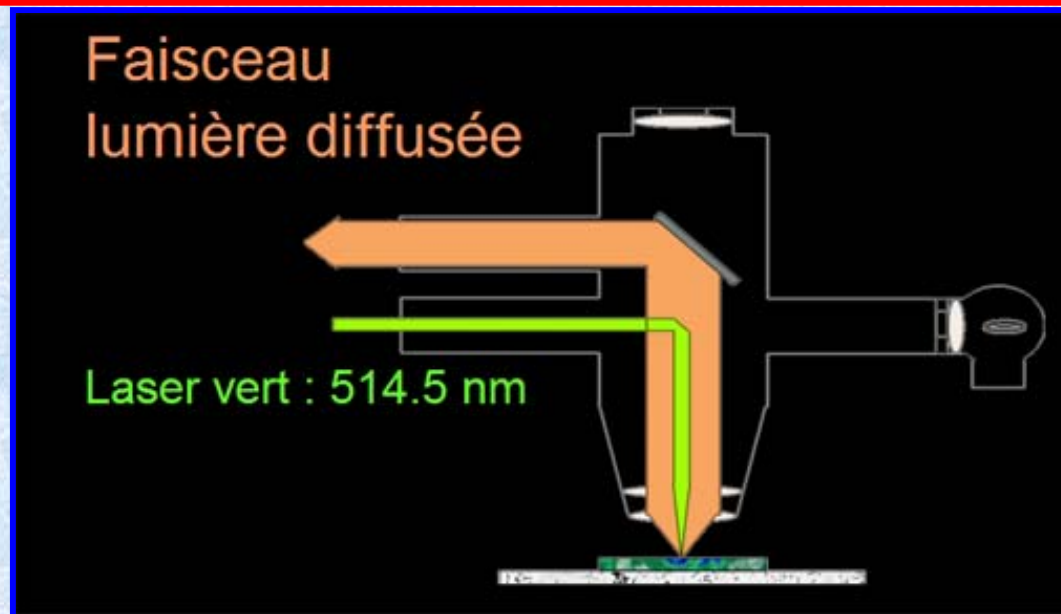
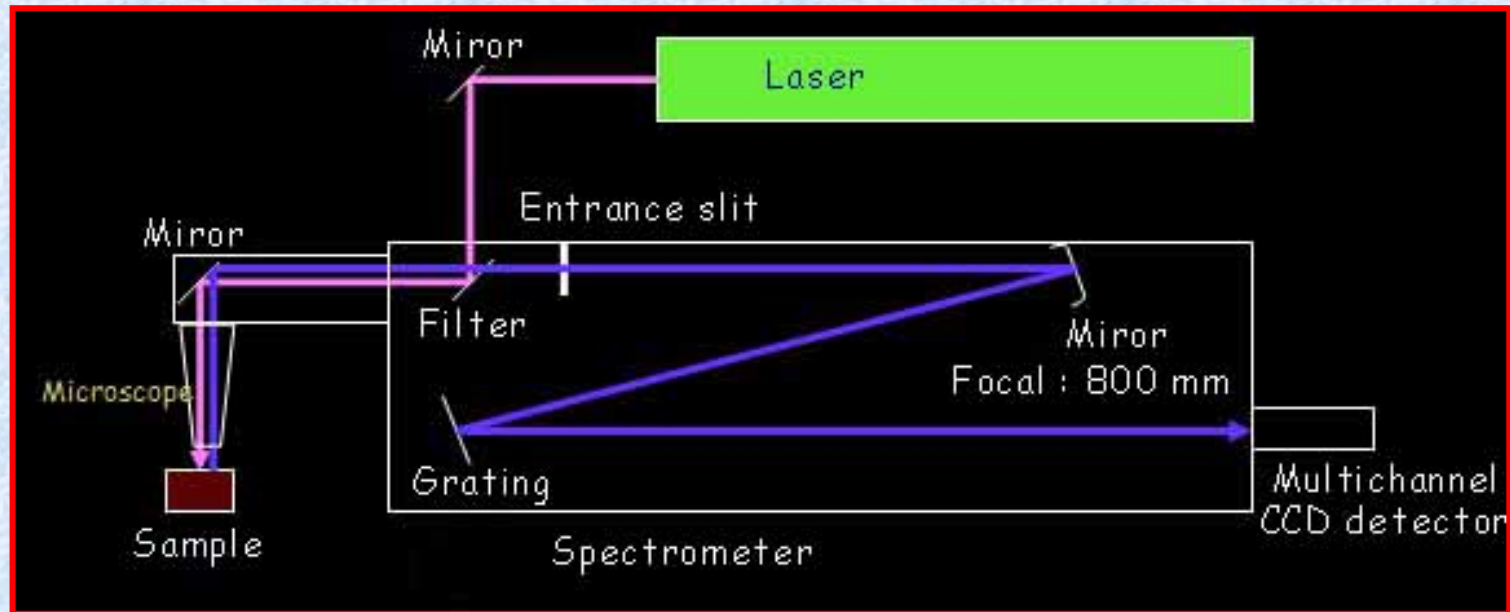
Near IR:

- (1) Can be operated at much higher power w/o causing photodecomposition of the sample.
- (2) Not energetic enough to populate a significant number of fluorescence-producing excited electronic state.

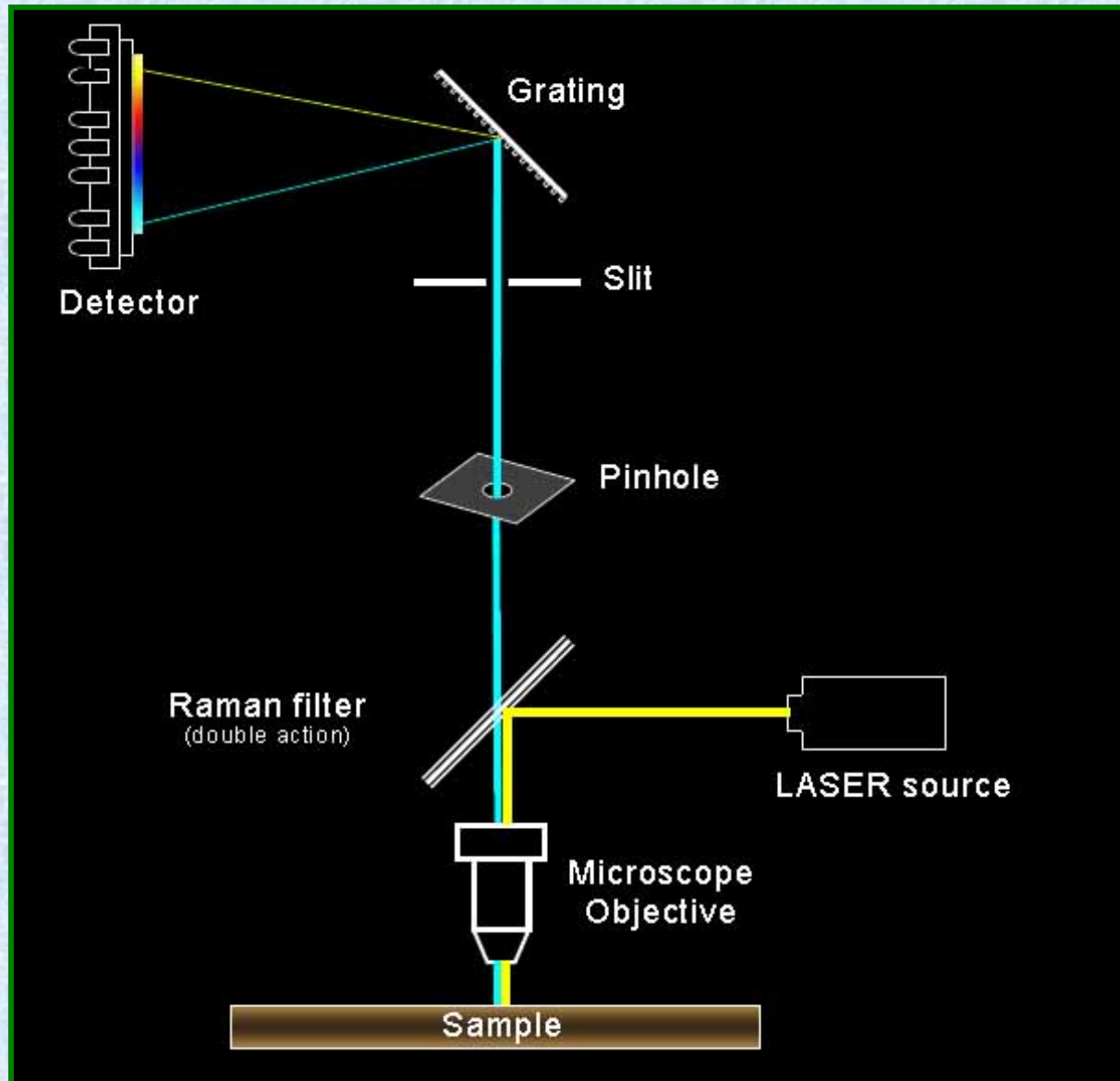
CW LASERS FOR ANALYTICAL RAMAN SPECTROSCOPY

Type	$\lambda(\text{nm}^a)$	Power (typical)
Doubled Ar ⁺	244, 257, 229	15–200 mW
Ar ⁺ (air cooled)	488.0, 514.5	5–50 mW
Ar ⁺ (water cooled)	351.1	0.1–10 W
	479.9	
	476.5	
	488.0	
	496.5	
	514.5	
	528.7	
He–Ne	632.8	5–100 mW
Kr ⁺	413.1	0.1–4 W
	647.1	
	752.5	
Nd:YAG	1064	0.1–10 W
Doubled Nd:YAG	532	0.05–5 W
Diode	670–865 nm	0.01–1 W

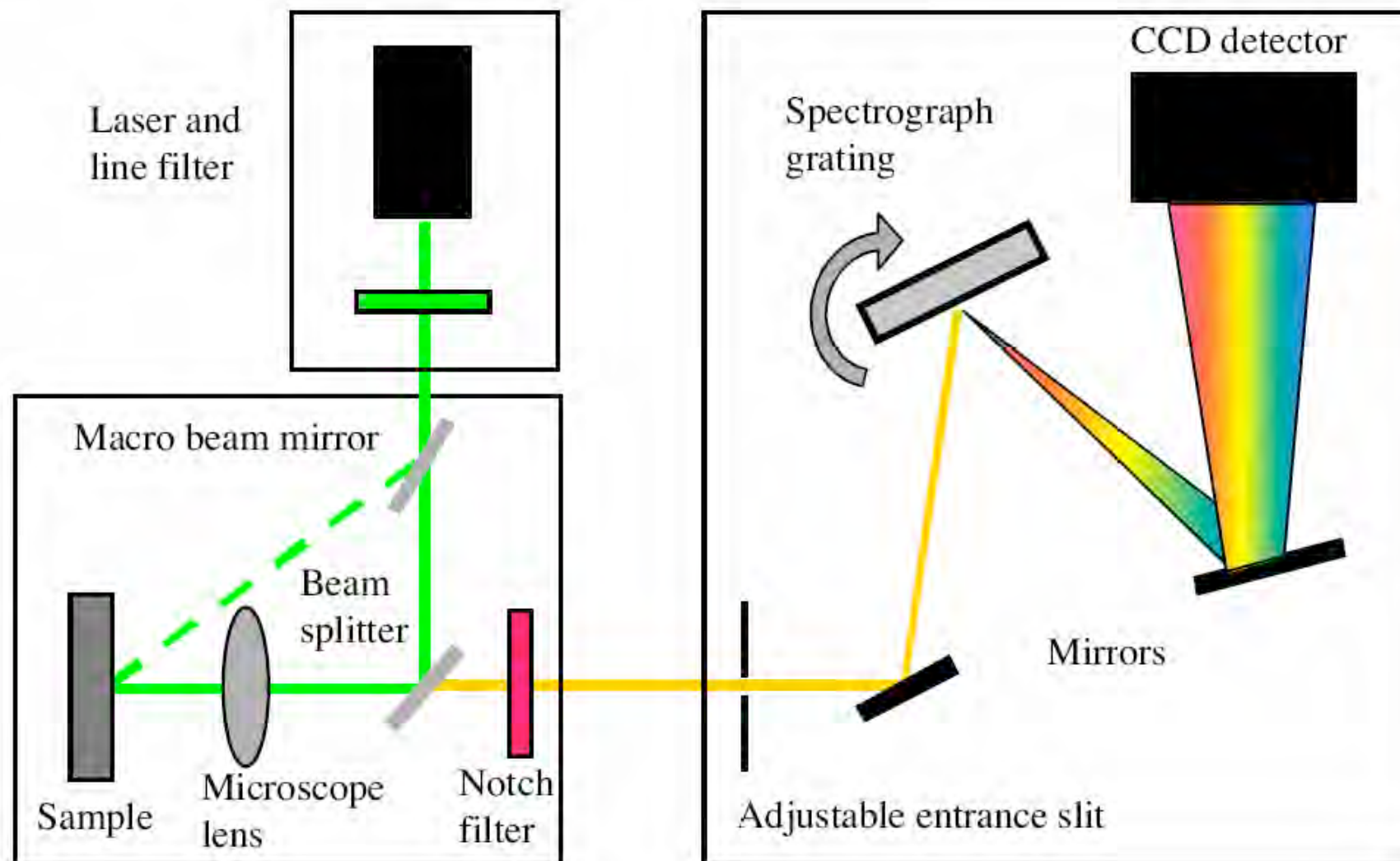
TECHNICAL DETAILS



TECHNICAL DETAILS

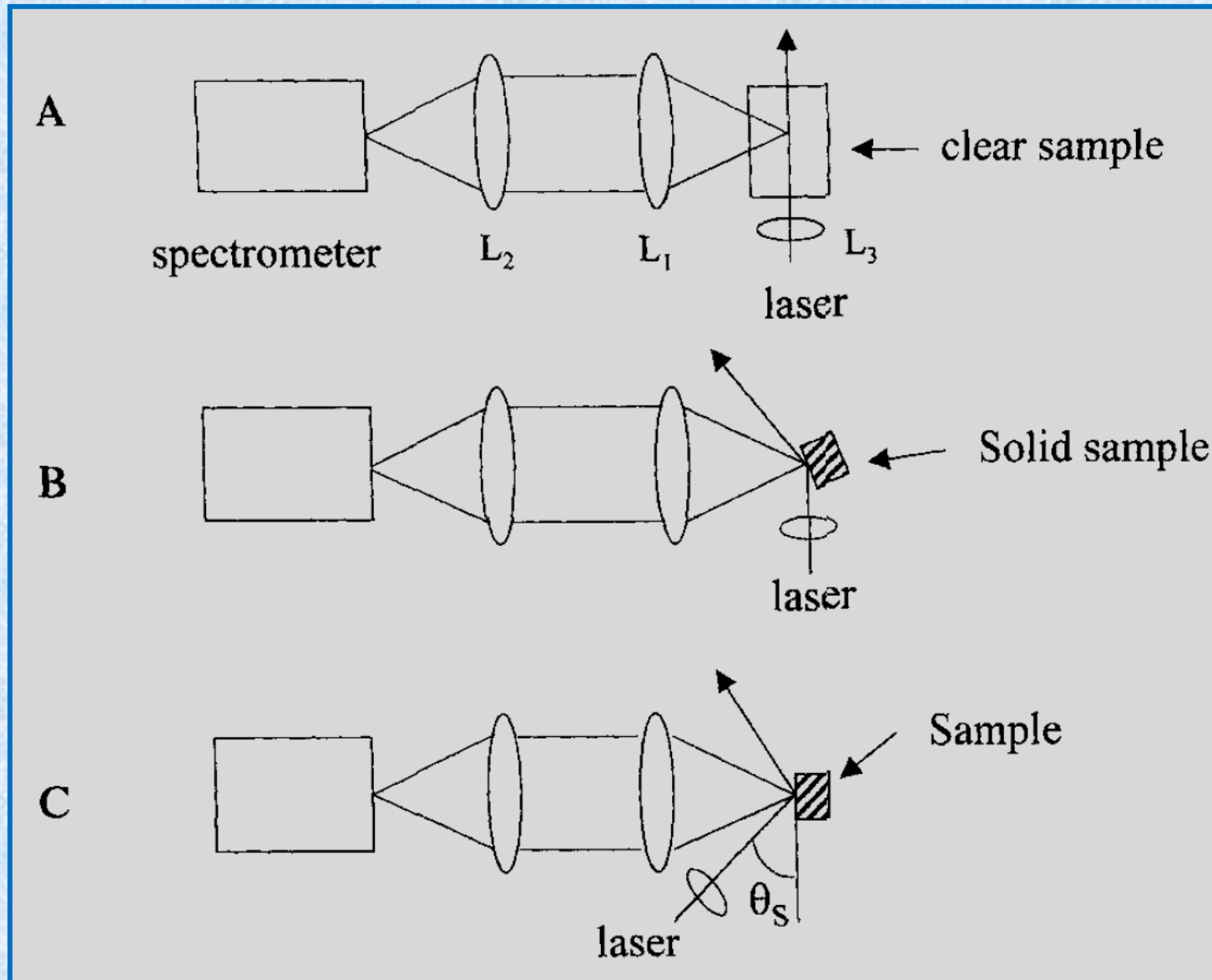


Simplified Raman spectrometer layout



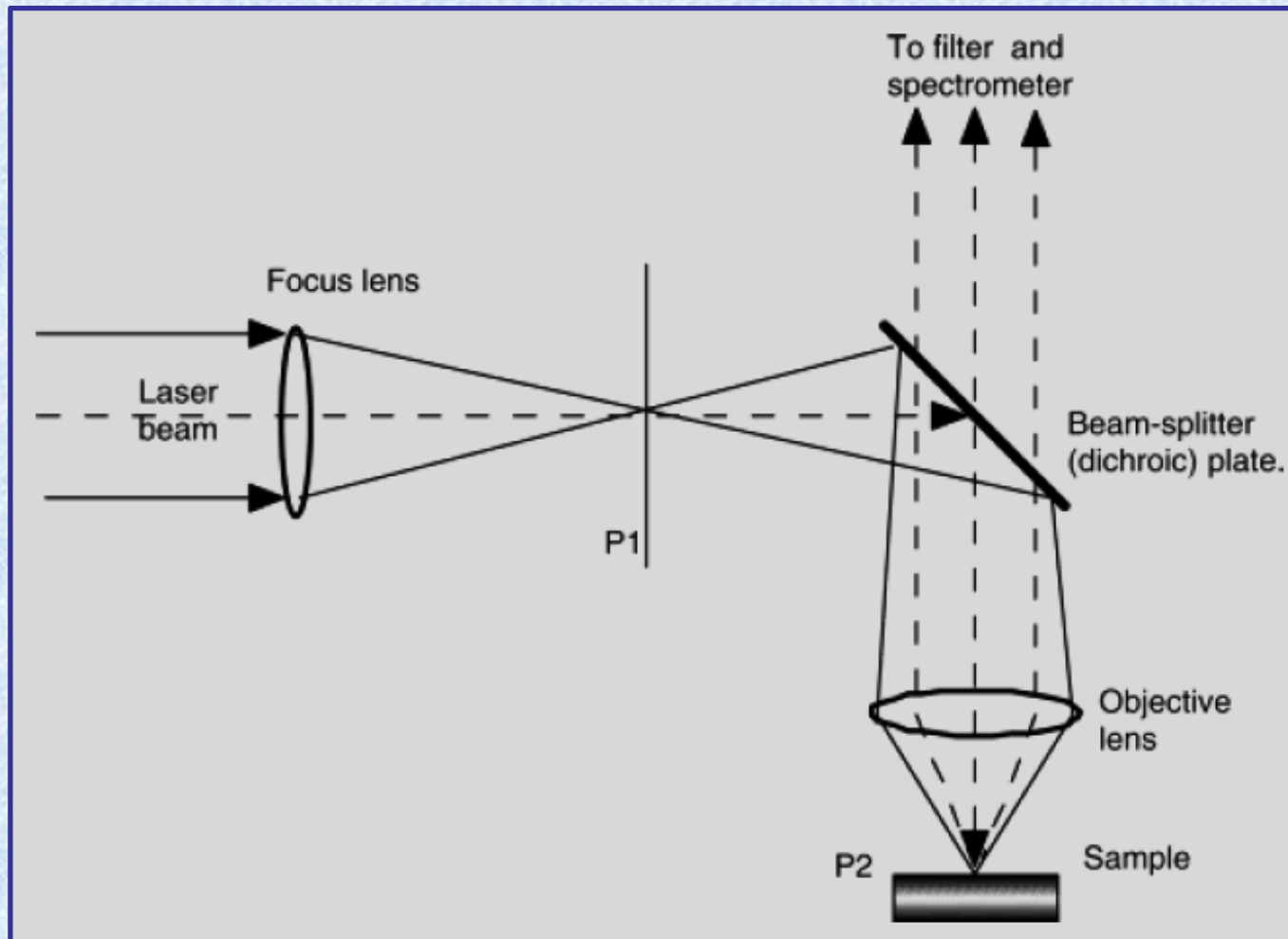
SCATTERING GEOMETRIES (1/3)

The Right-Angle 90° Geometry



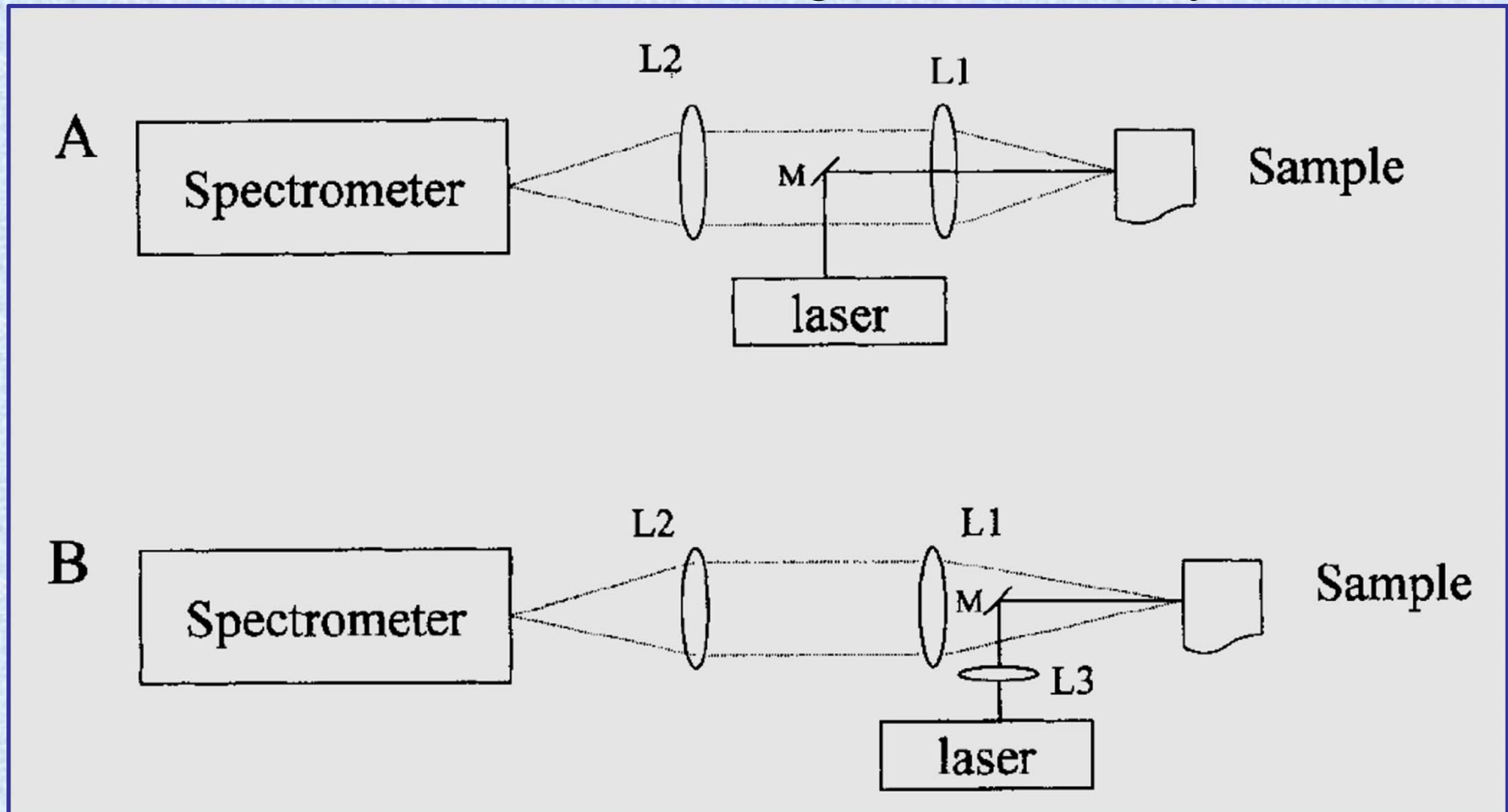
SCATTERING GEOMETRIES (2/3)

The Back-Scattering (180°) Geometry

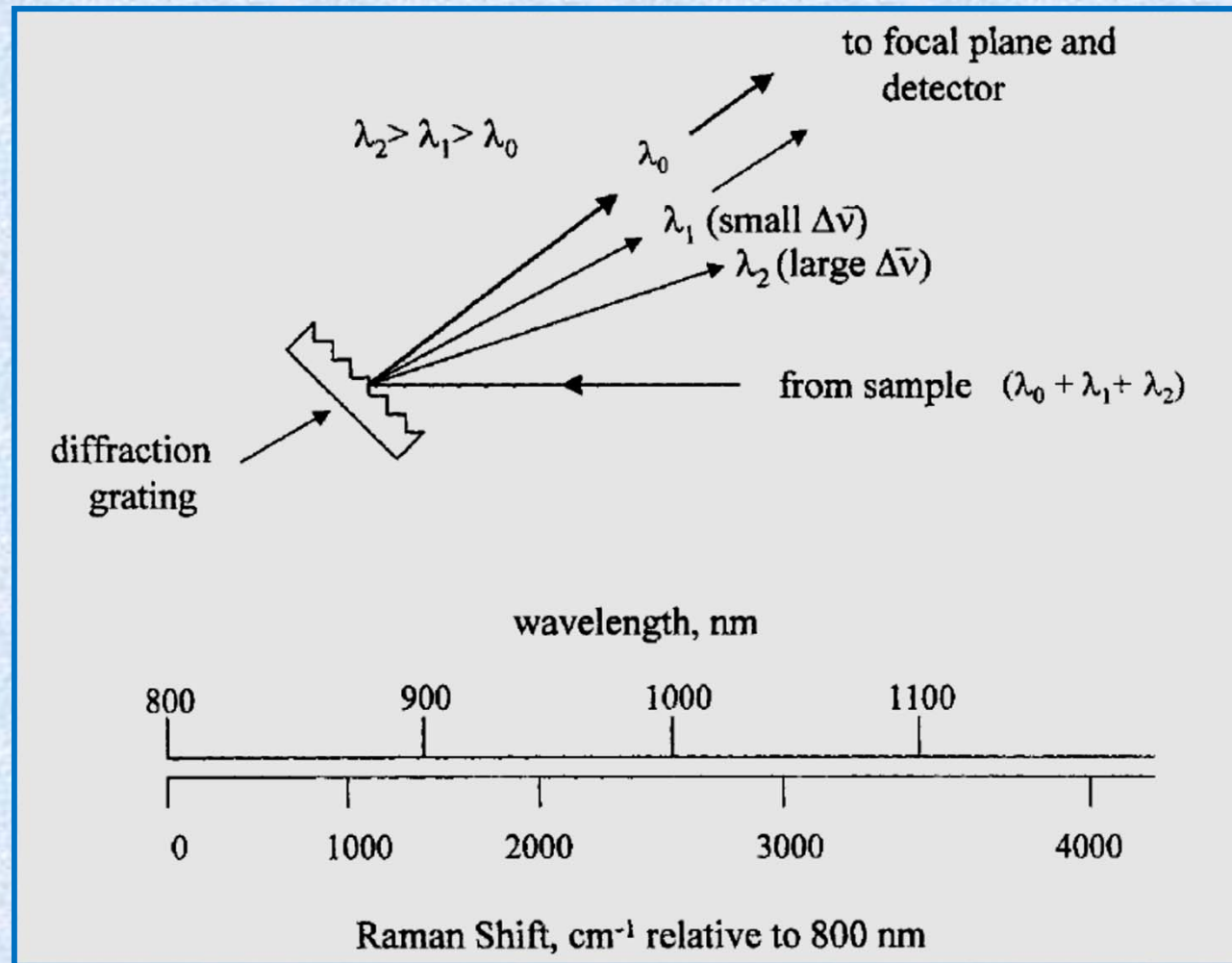


SCATTERING GEOMETRIES (3/3)

The Back-Scattering (180°) Geometry



DISPERSIVE RAMAN SPECTROMETERS



Wavelength analyzer: is a subunit within a Raman spectrometer that allows separation of wavelengths and eventually Raman shifts.

Gratings disperse the light according to *wavelength*, not *wavenumber*, resulting in a linear spread of wavelengths at the focal plane of the spectrometer.

DISPERSIVE RAMAN SPECTROMETERS

Relation between *wavenumber* and *wavelength*

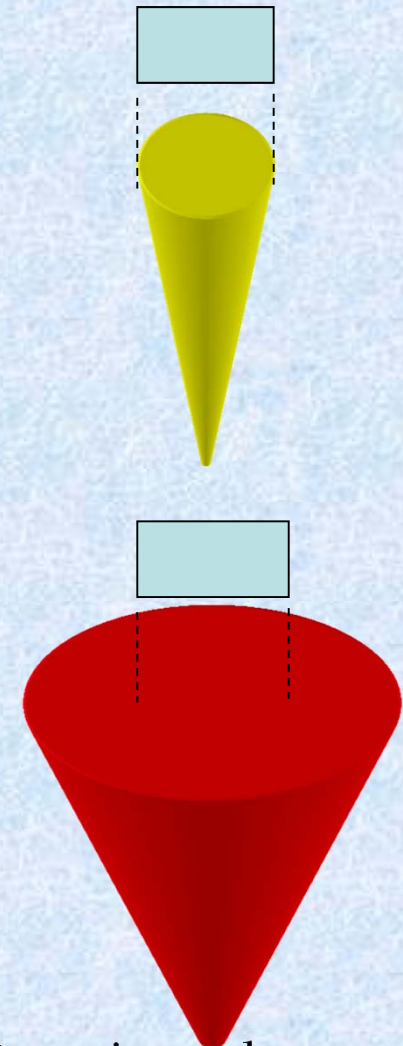
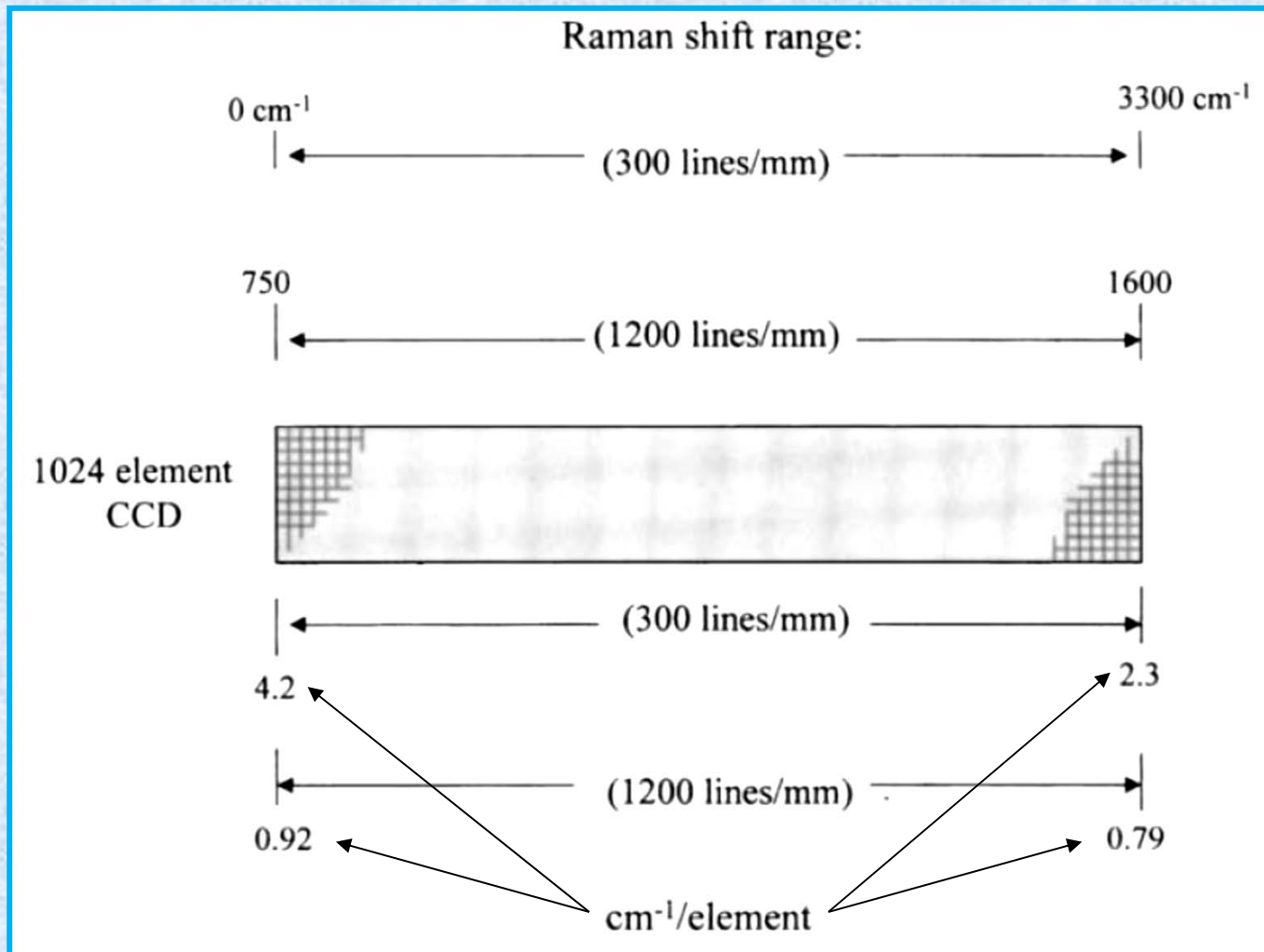
$$d\tilde{\nu} = \frac{1}{\lambda^2} d\lambda$$

For example, the 10 nm between 800 and 810 nm contain 154 cm⁻¹, while the range 1000 to 1010 nm contains only 99 cm⁻¹. [420 cm⁻¹ 488-498nm]

A slit width sufficient to collect **0.1 nm** at **800 nm** will also collect **0.1 nm** at **1000 nm**. But the same slit will collect 1.6 cm⁻¹ at 800 nm and 1.0 cm⁻¹ at 1000 nm.

- A *spectrograph* disperses light along a *focal plane*.
- A spectrograph with a multichannel detector at the focal plane is a key component in a *multichannel spectrometer*.
- If an exit slit is placed at the focal plane, a small range of wavelengths (*bandpass*) is transmitted; the device is a *monochromator*.

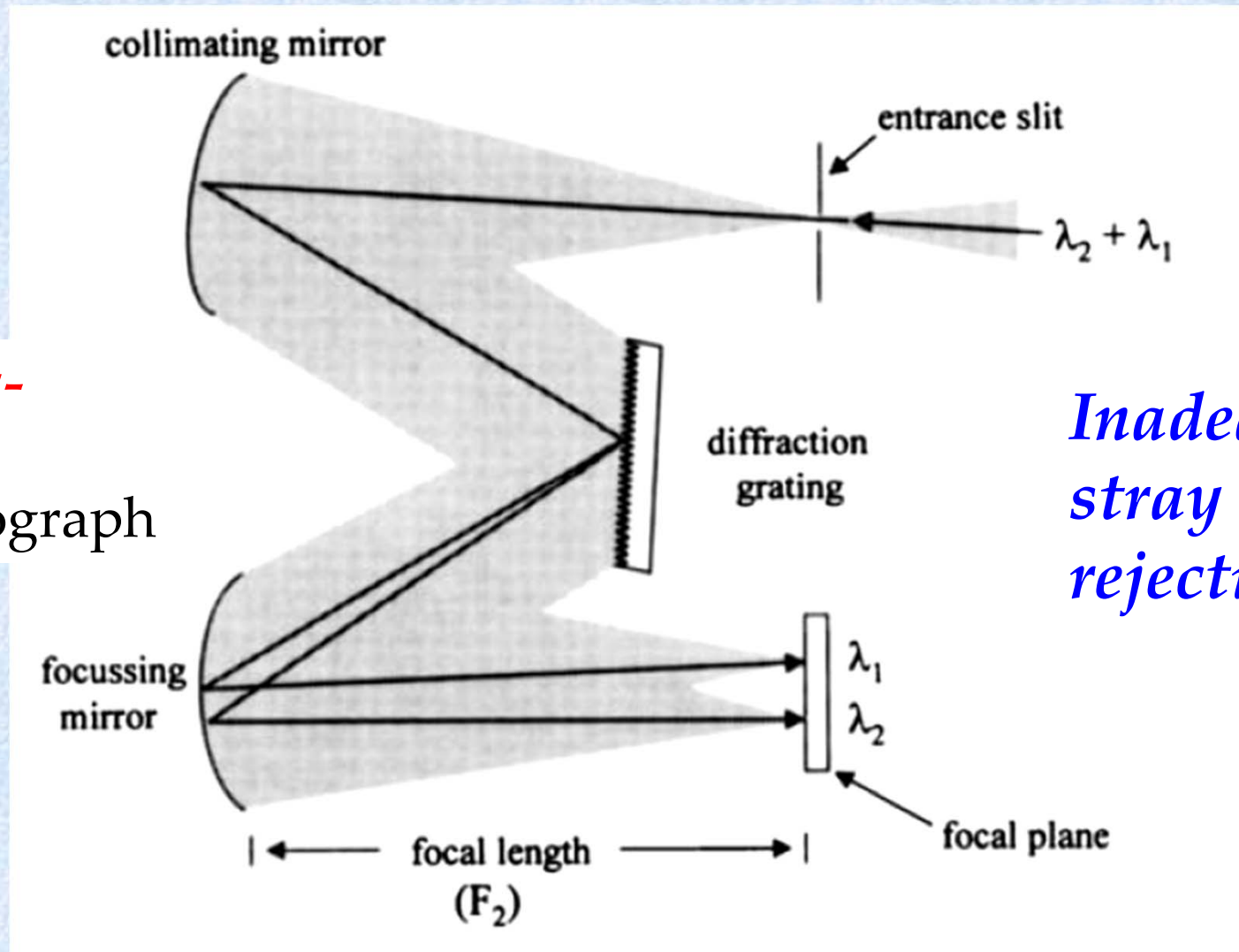
DISPERSIVE RAMAN SPECTROMETERS



Dispersion. The linear dispersion (mm / nm) is often converted to reciprocal linear dispersion (dn / dl , units of nm/mm).

It describes how much of the spectrum (in nanometers) is covered in a unit of focal plane.

DISPERSIVE RAMAN SPECTROMETERS

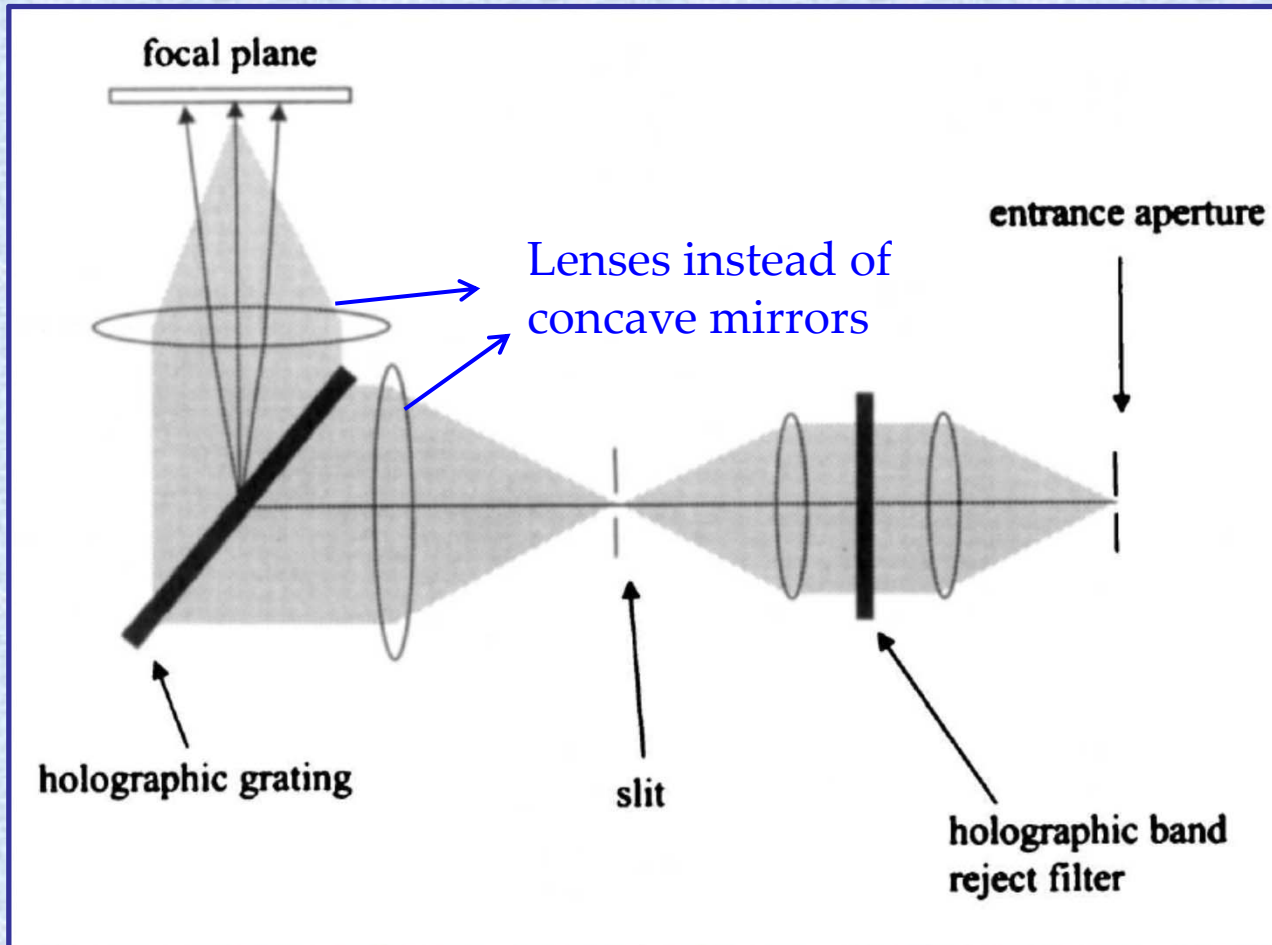


Czerny-Turner
spectrograph

*Inadequate
stray light
rejection*

Transmission: The transmission of the wavelength analyzer is the fraction of light of a given wavelength entering the entrance slit that reaches the detector.
Unitless; 5-60%; The largest transmission losses usually occur at the grating.

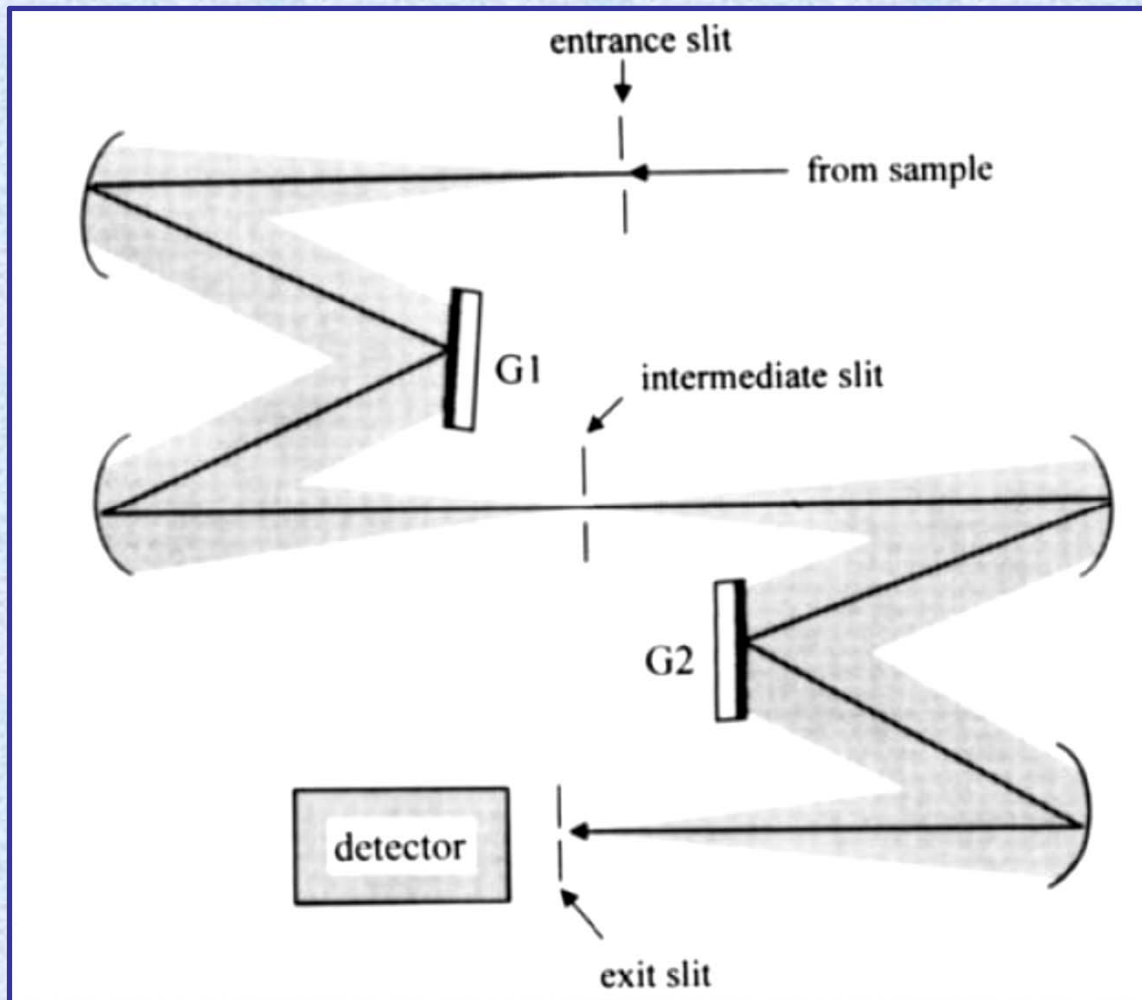
HOLOGRAPHIC GRATINGS



- ✓ The optical axis is normal to the lenses, significantly reducing optical aberrations and maintaining image quality.
- ✓ The transmission design improves grating efficiency, leading to high spectrograph transmission.
- ✓ Low aberrations result in a relatively large flat field and good compatibility with CCD detectors.

- Consists of layers of **photoactive emulsion** between glass or quartz plates, which are exposed to interference patterns that generate a holographic image in the emulsion.
- The image consists of variations in refractive index that can be patterned to form a diffraction grating.

DOUBLE MONOCHROMATORS

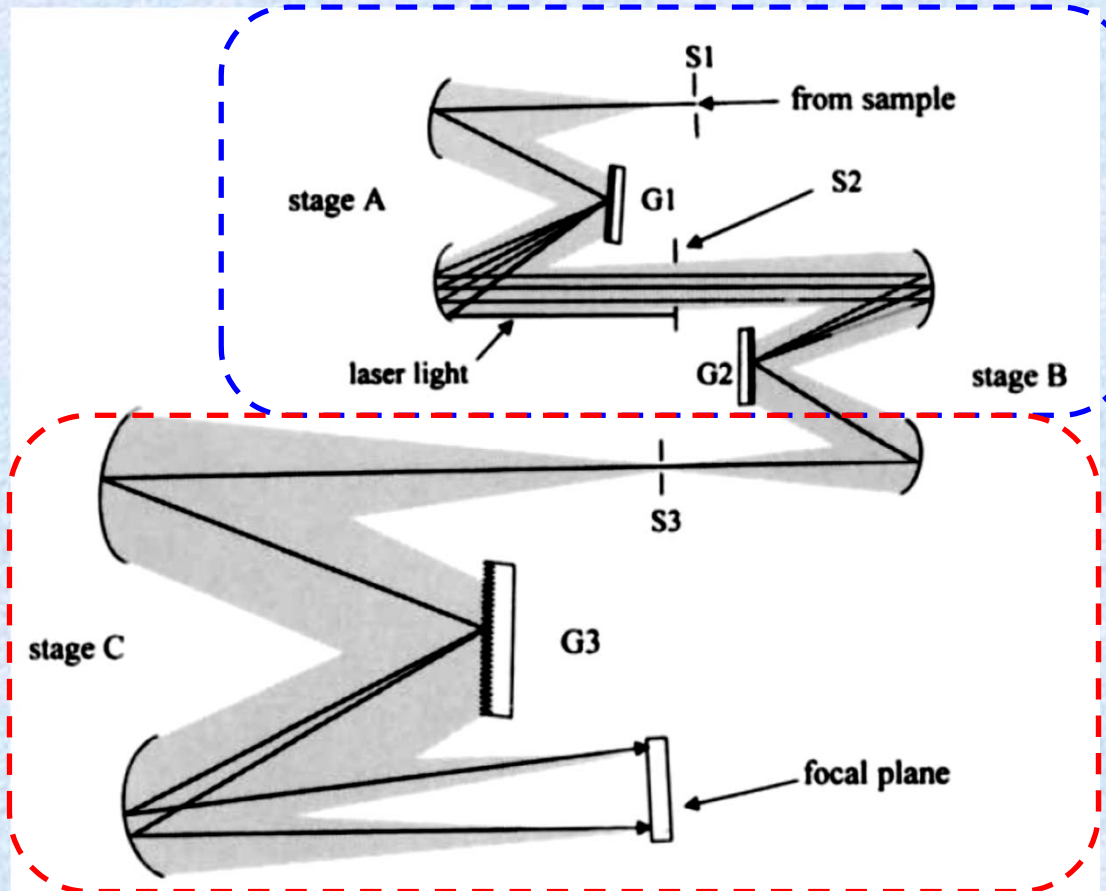


Additive dispersion

The two gratings are typically scanned synchronously and each Raman shift increment is collected in series.

- Combining two single-grating monochromators in series, with a common “intermediate” slit, *the light is dispersed twice*; the bandpass can be quite narrow.
- Very efficient stray light rejection permits approaching the Rayleigh line.

TRIPPLE MONOCHROMATORS



Pre-monochromator:

Rejection of Rayleigh light without further analysis of the scattered light.
(Tunable bandpass filter)

$$S1 \equiv S3$$

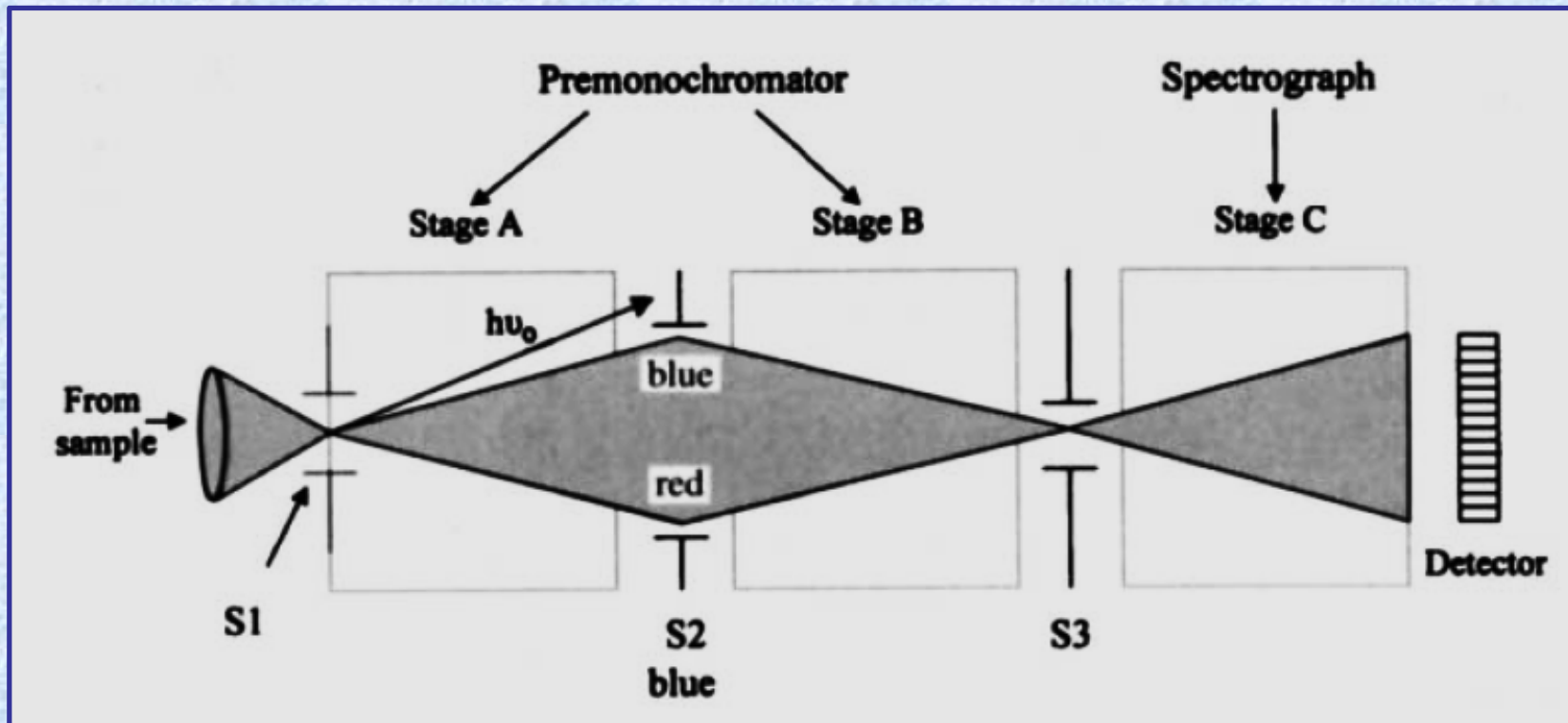
Spectrograph:

Analysis of the scattered light that does not contain the Rayleigh component

5-10% transmission

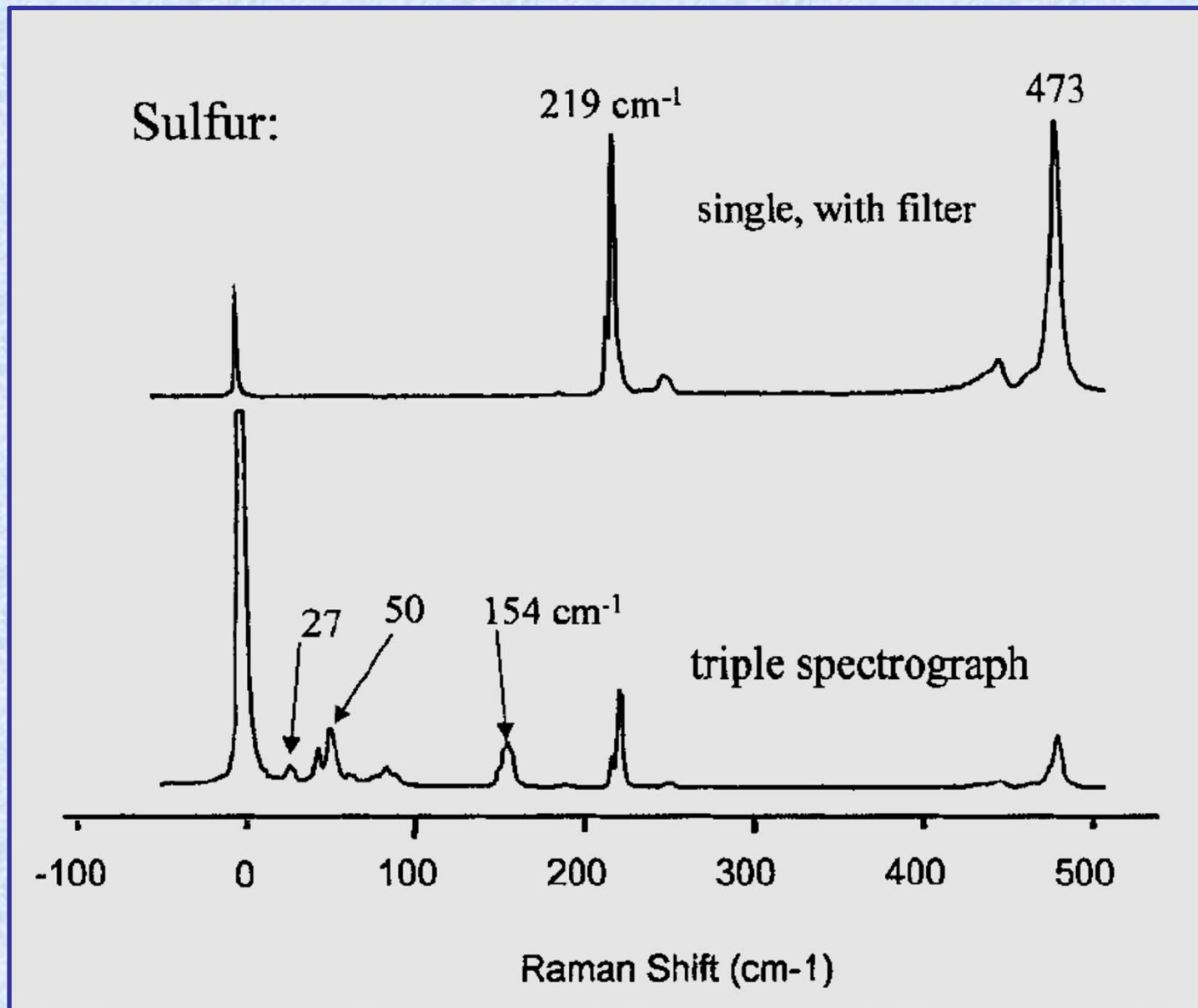
- Stages A and B comprise a tunable filter that is configured as a **subtractive dispersion** double monochromator.
- Stage A disperses the light onto an intermediate "slit" S2 that blocks all but a certain wavelength range.
- Stage B is configured to recombine this range of wavelengths and focus them on the spectrograph entrance slit S3.

TRIPPLE MONOCHROMATORS



- Stage A disperses the light onto an intermediate slit S2, which is usually wide enough to transmit the entire wavelength range of interest. This range does not include the laser wavelength, however, **much of the elastic scatter is blocked at S2.**
- Stage B recombines the light transmitted by S2 (so-called “subtractive dispersion”) to focus to a point at S3.
- Stage C then disperses this filtered light onto the detector.

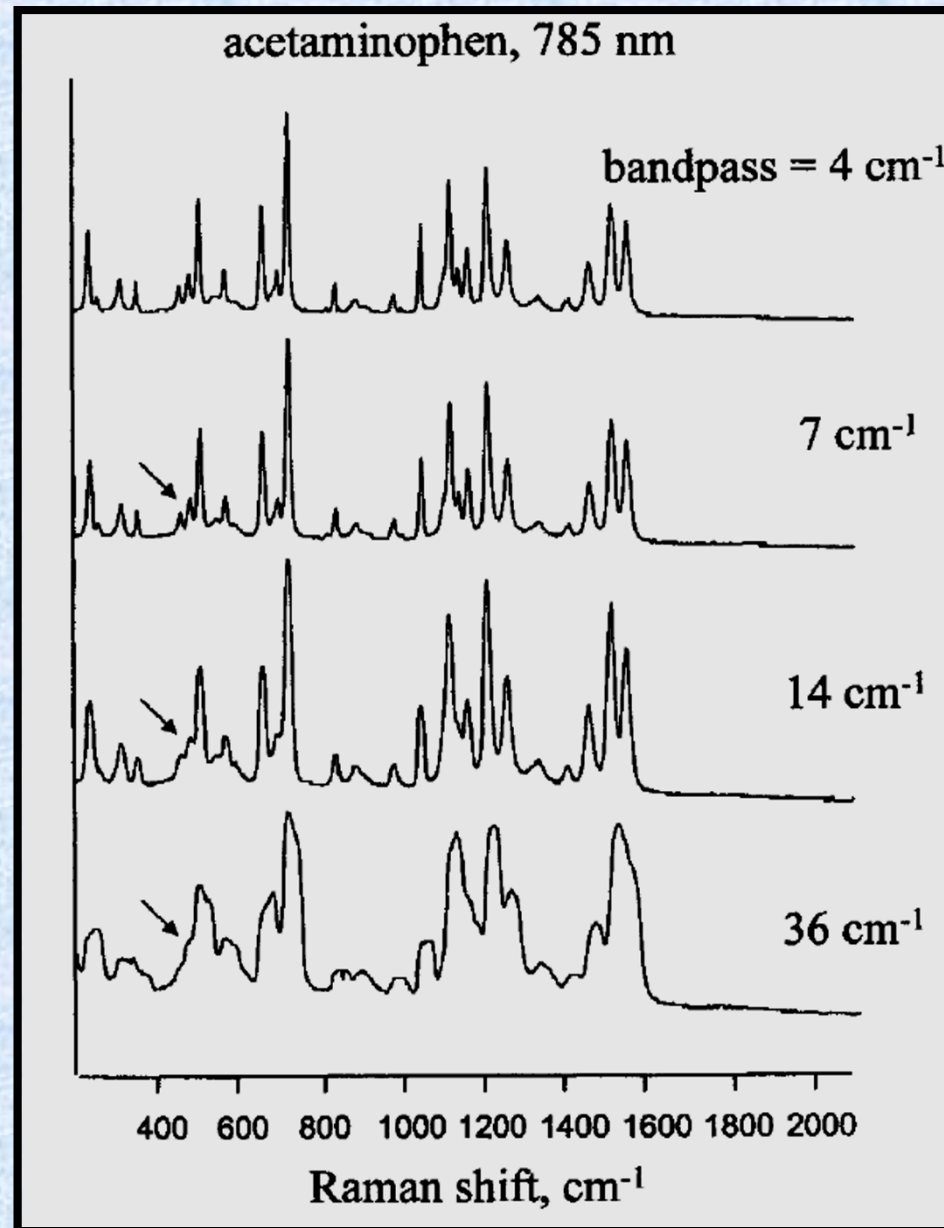
PERFORMANCE COMPARISON



RESOLUTION ASPECTS

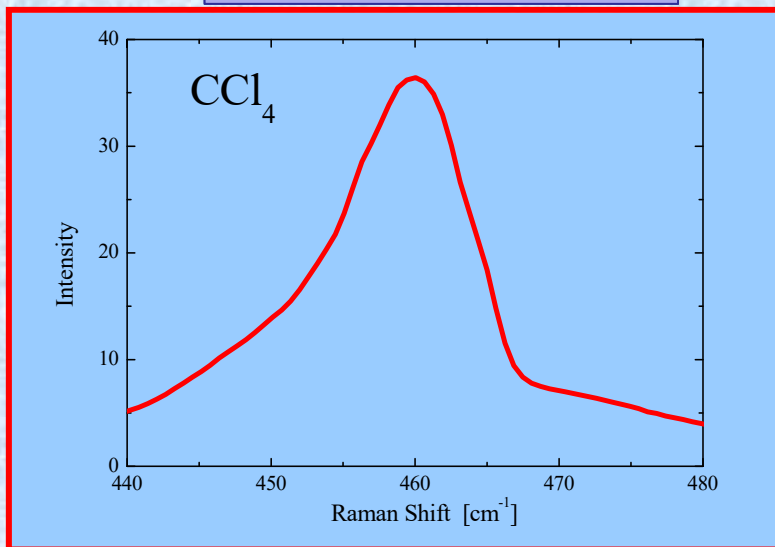
Resolution:

The ability to distinguish closely spaced Raman peaks

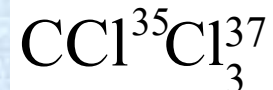
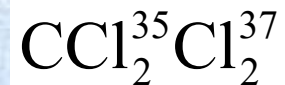
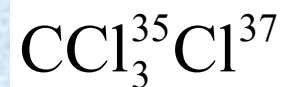
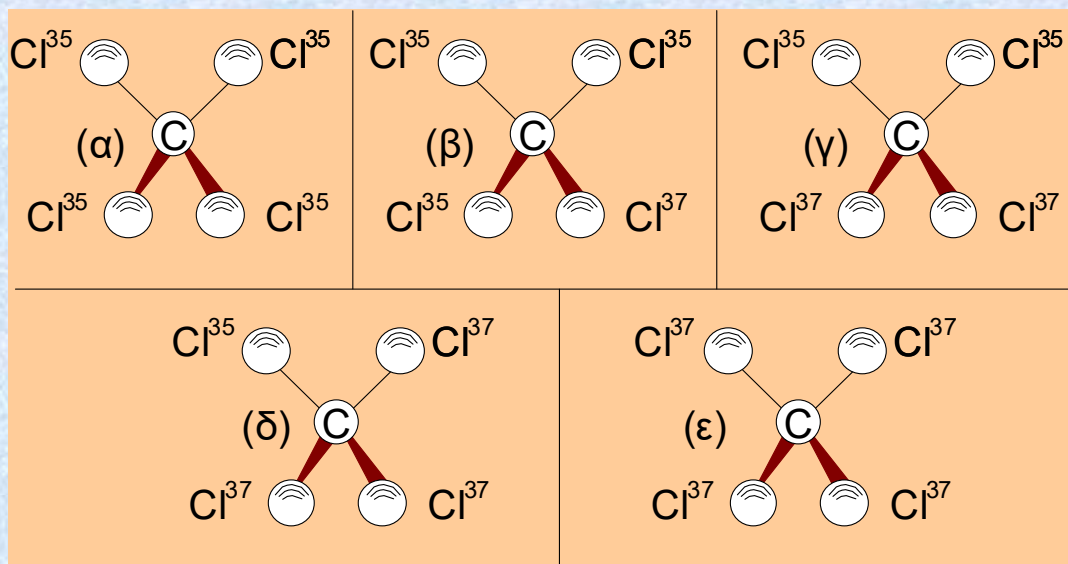
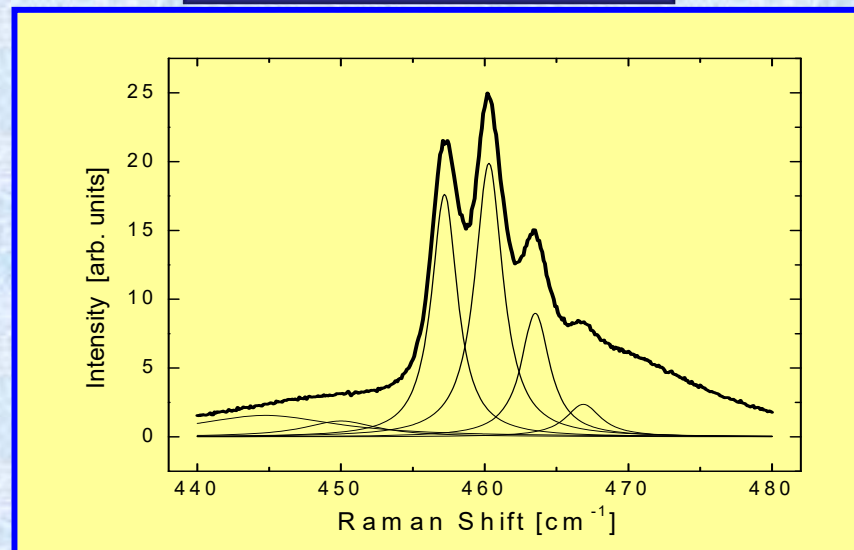


RESOLUTION ASPECTS

Low resolution

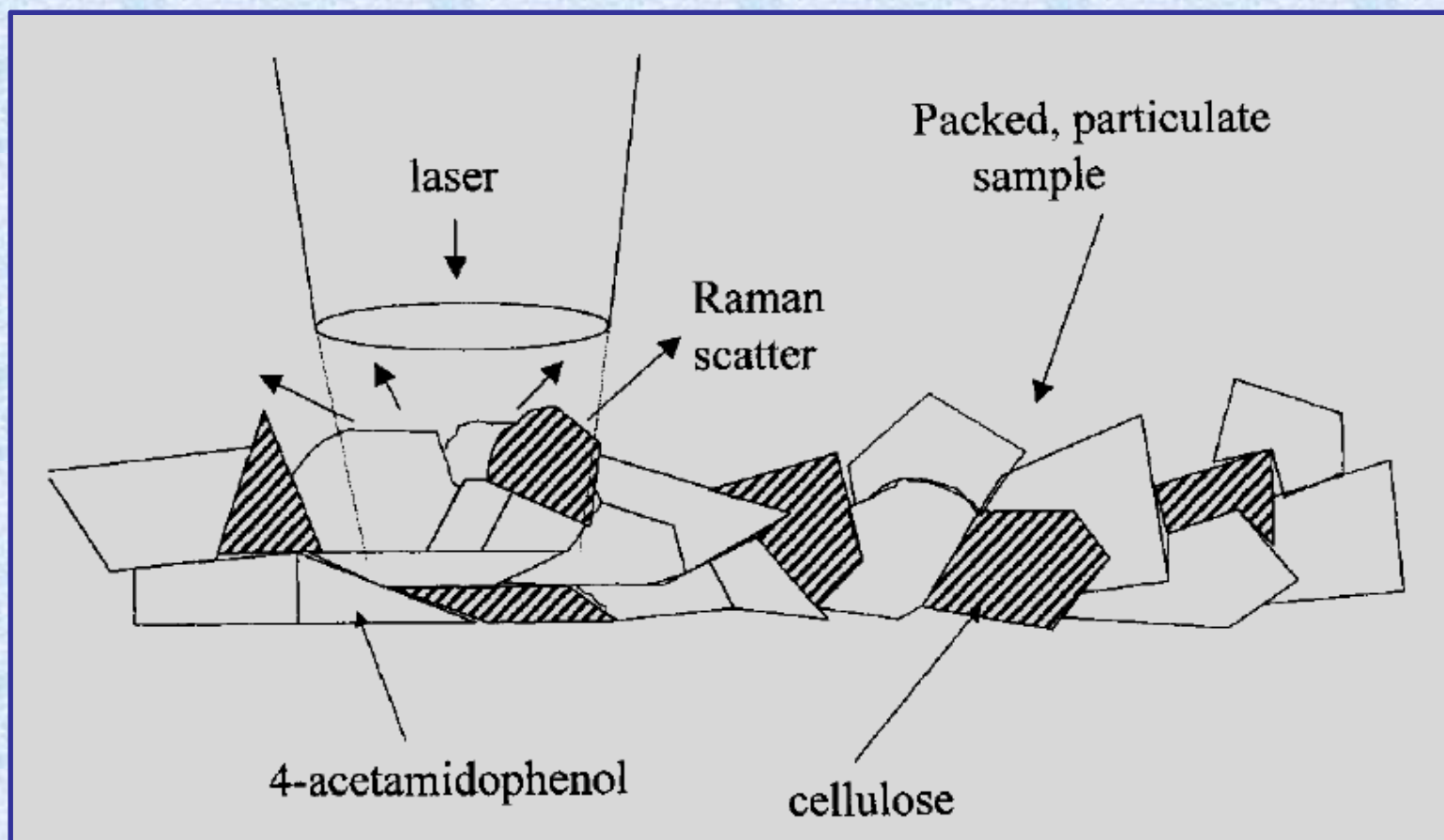


High resolution

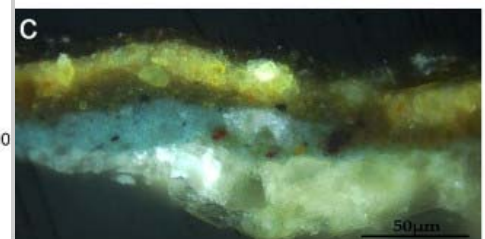
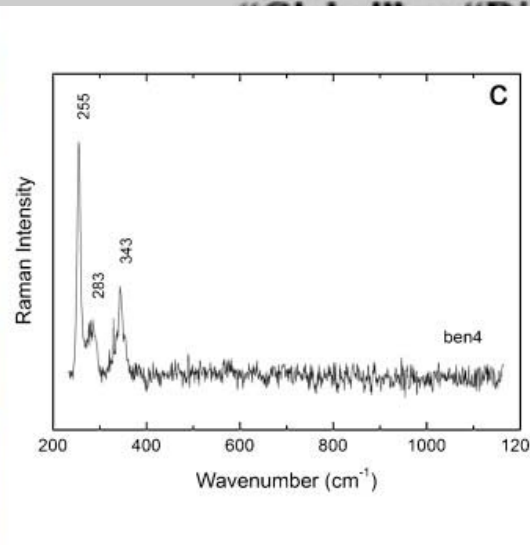
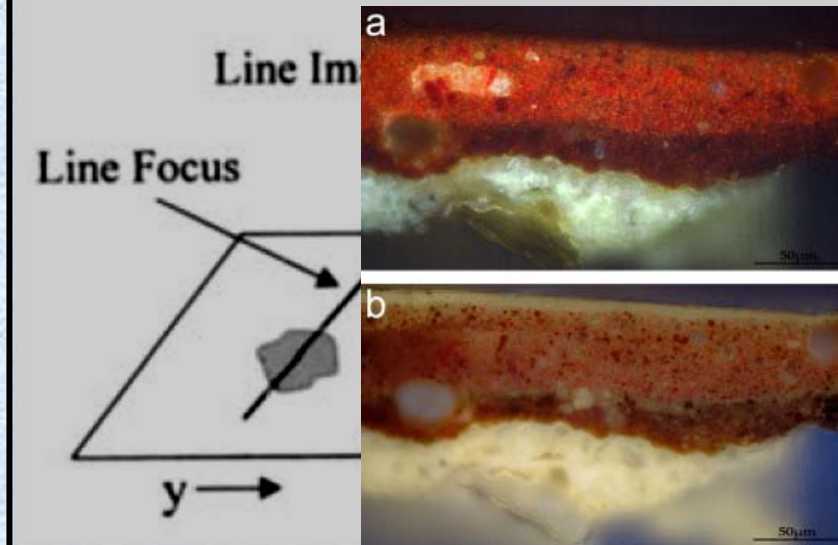
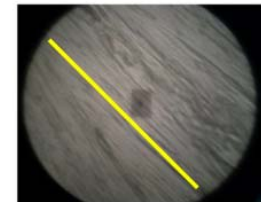
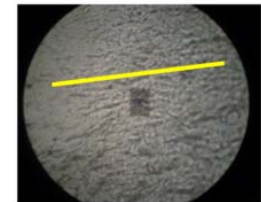
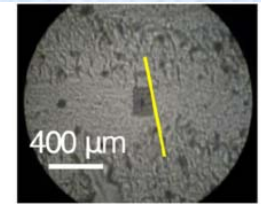
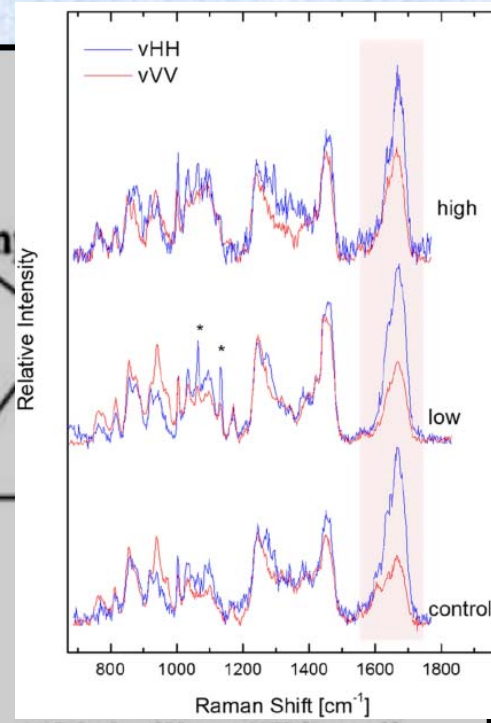
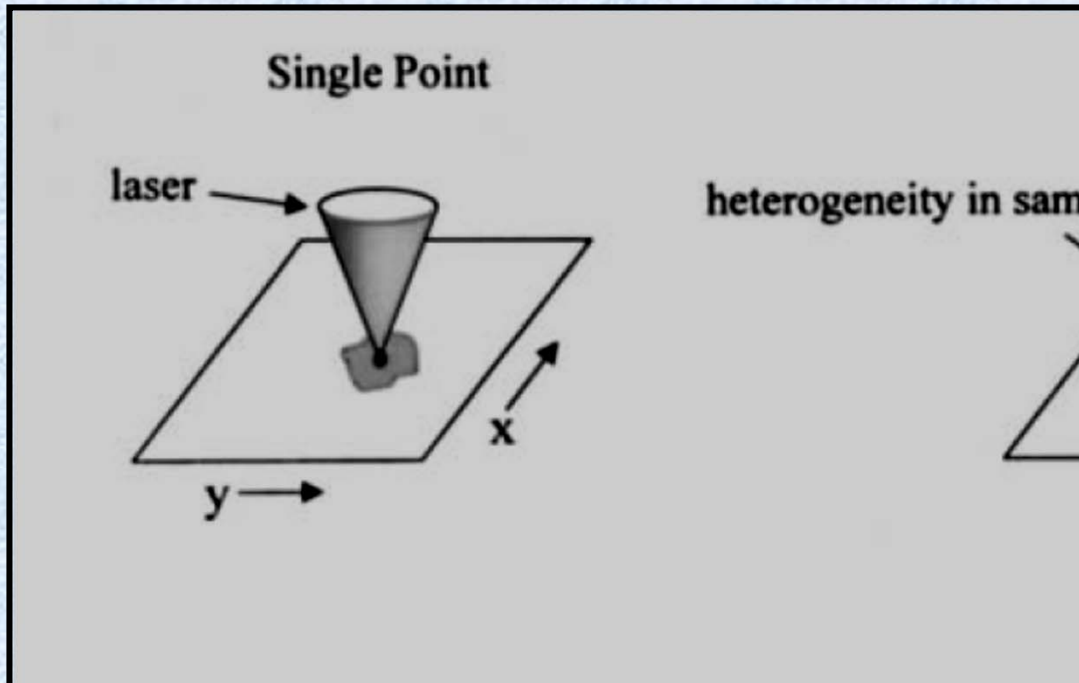


SAMPLE HETEROGENEITY

Back-scattering geometry:
source of irreproducibility when dealing with solid samples



SAMPLE HETEROGENEITY

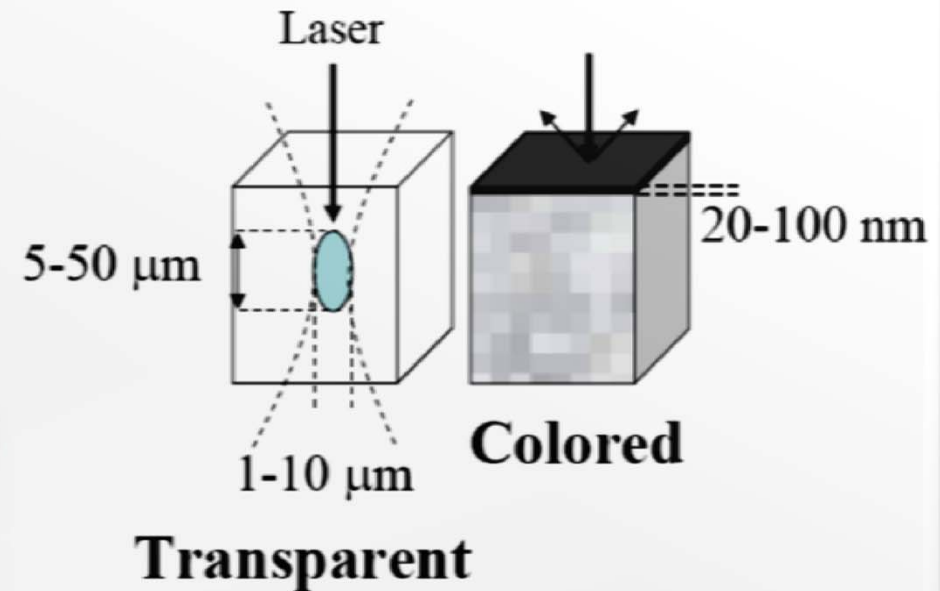
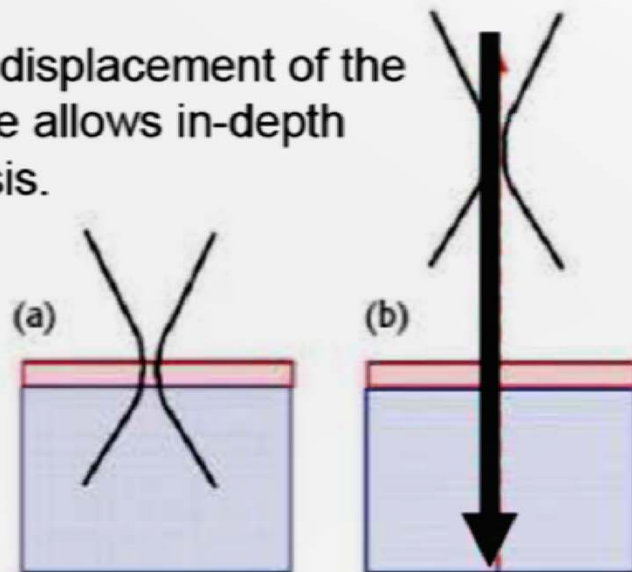


CONFOCAL RAMAN SPECTROSCOPY

Confocal analysis/depth (z) imaging

Goal: increase the spatial resolution

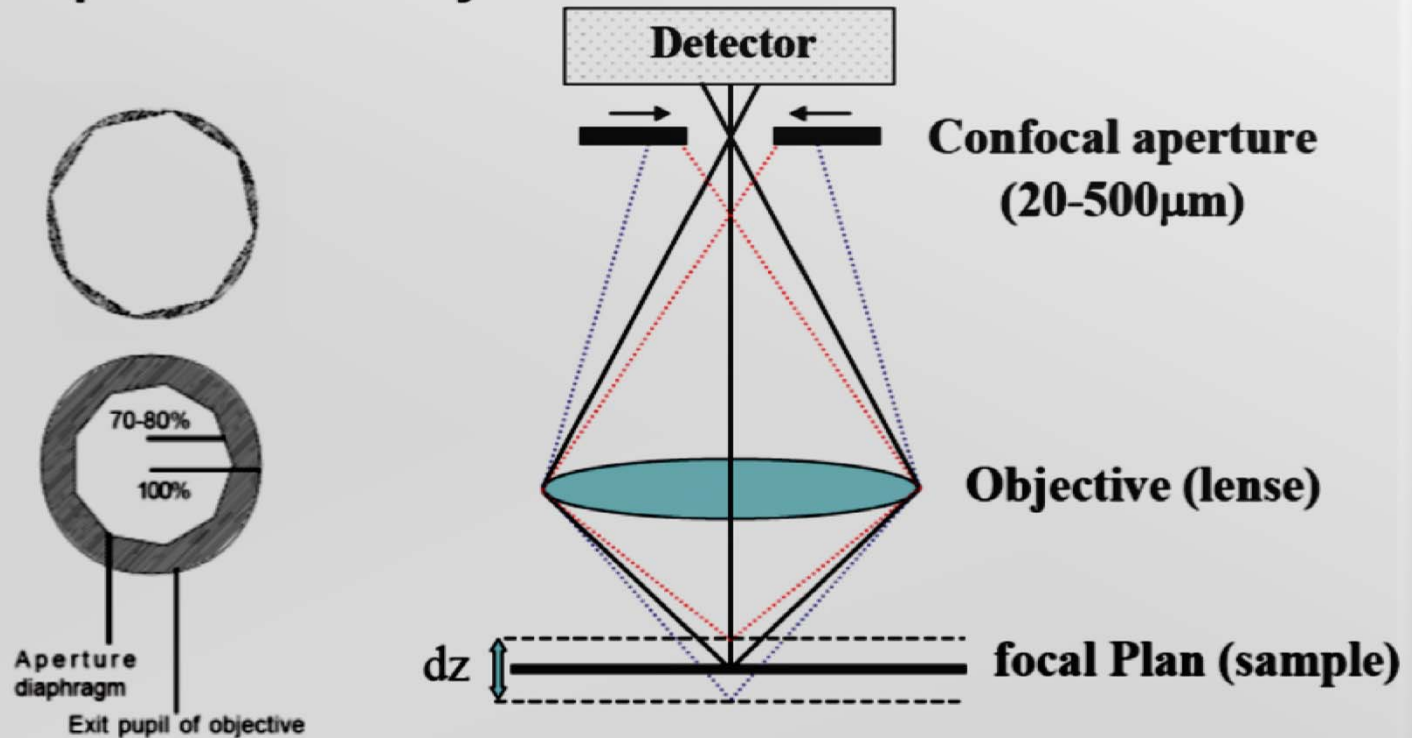
The z displacement of the sample allows in-depth analysis.



Confocal imaging is only relevant for optically clear materials

CONFOCAL RAMAN SPECTROSCOPY

General principle of confocality

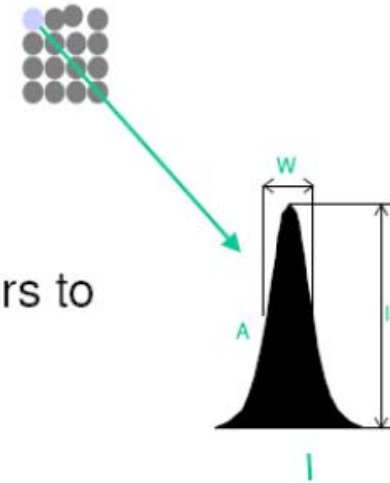


Out of focal plan light is stopped by the confocal aperture before reaching the detector

RAMAN MAPPING

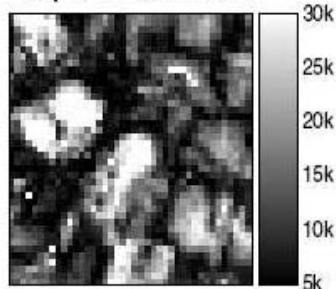
Basic principle*

- At each point (x,y)
 - Take spectrum
 - Fit curve(s)
- Use curve parameters to make images
 - Area(x,y) etc.



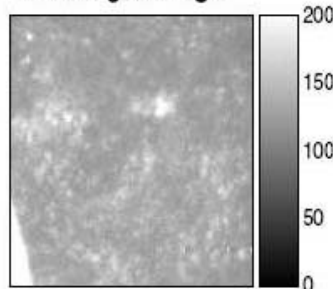
CVD Diamond

Map 1332 cm^{-1} band



40 μm

White light image

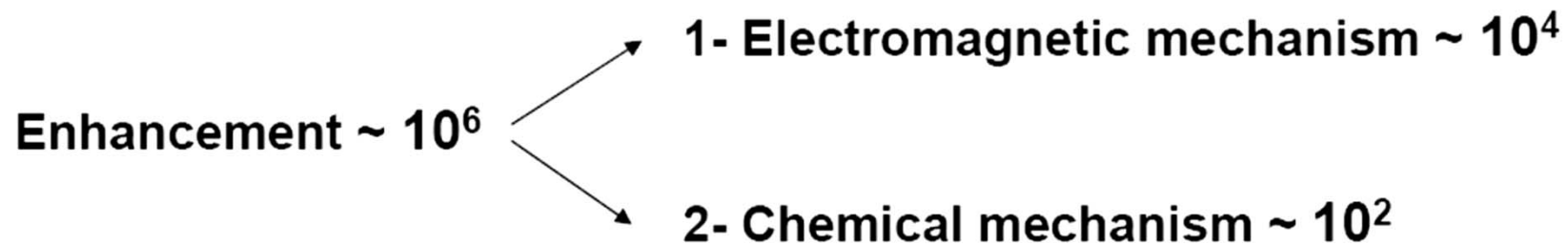


40 μm

**The sample is moving (not the laser).
X-Y steps $\geq 0.1 \mu\text{m}$
Each point contains a full spectrum
 \Rightarrow All the spectral parameters
(intensity, width, position) can be
extracted and mapped**

SURFACE ENHANCED RAMAN SCATTERING (SERS)

SERS provides greatly enhanced Raman signal from Raman active molecules that have been adsorbed onto certain *metal surfaces*.



3- Giant enhancement $\longrightarrow 10^{10}-10^{16} ! \Rightarrow$ Single molecule detection (SM-SERS)

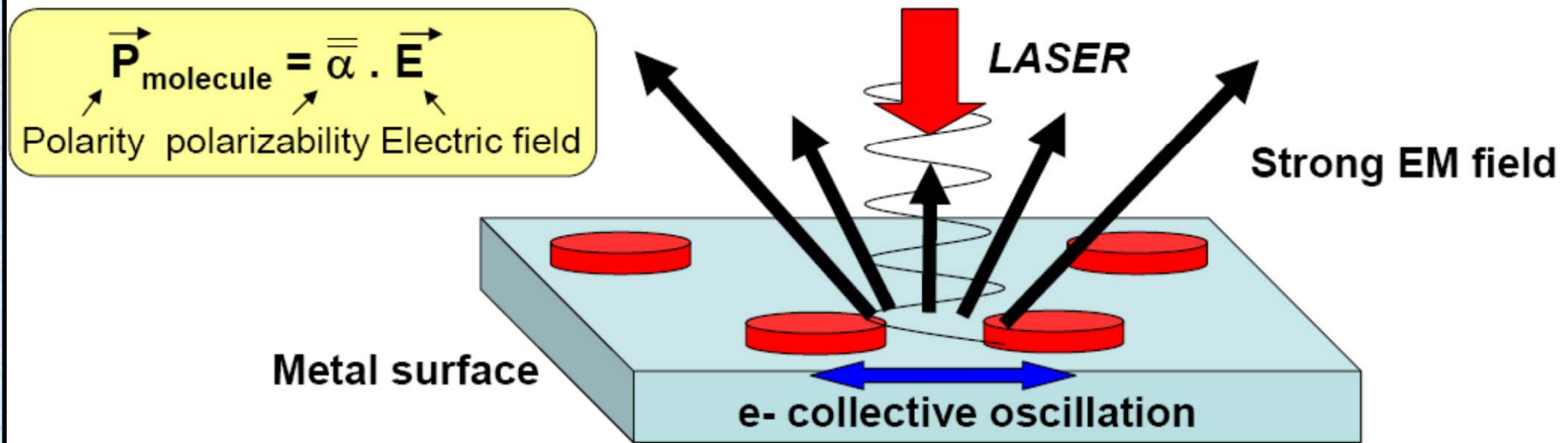
SURFACE ENHANCED RAMAN SCATTERING

What are the Enhancement mechanisms?

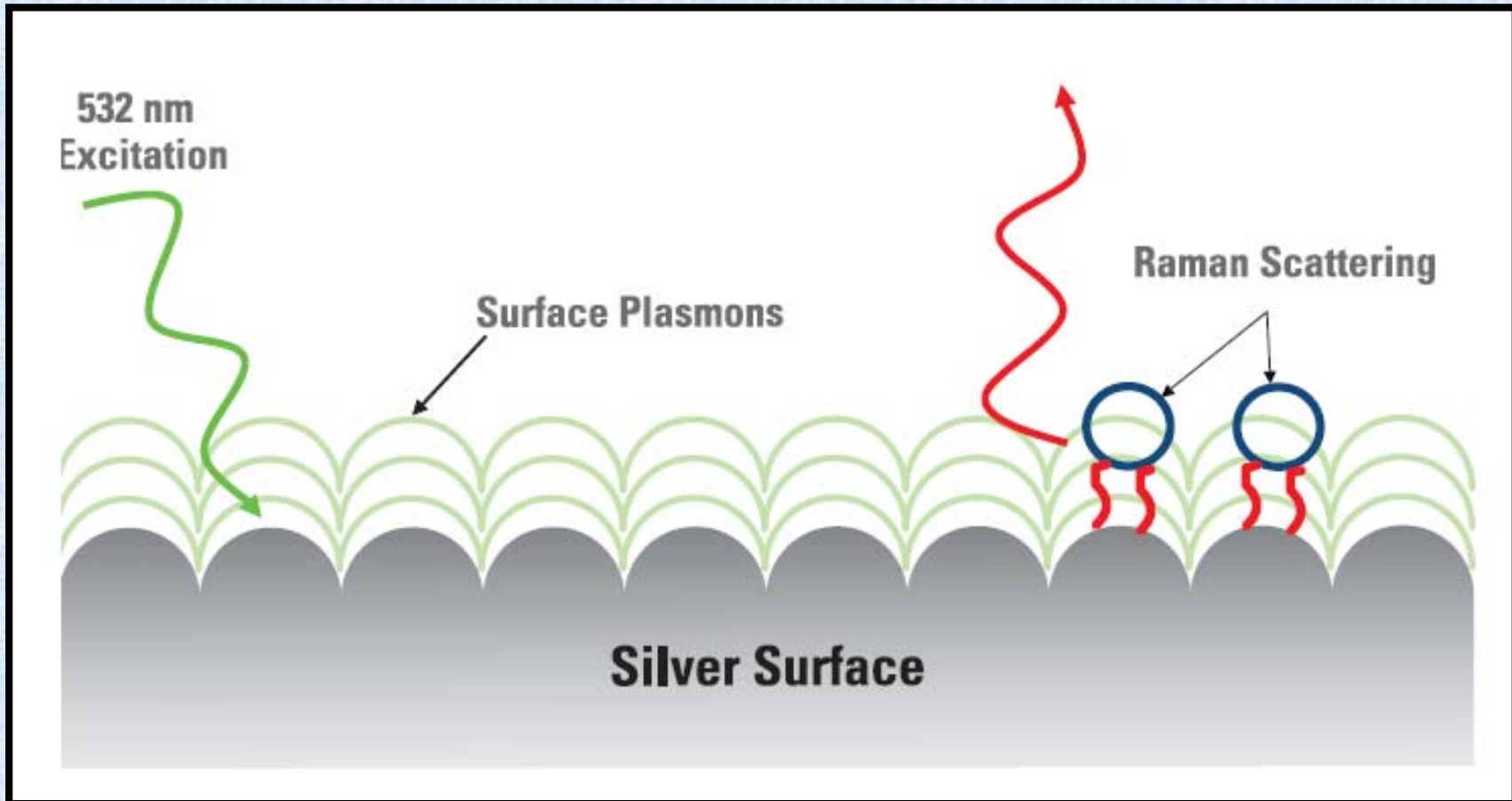
1- The electromagnetic enhancement mechanism (EM)

If the **correct** wavelength of light (laser) strikes a metallic roughness feature, the **plasma of conduction electrons** will oscillate collectively.

This collective motion creates a large EM field around the roughness feature. If a molecule is placed within the EM field, its own scattering is enhanced



SURFACE ENHANCED RAMAN SCATTERING



SURFACE ENHANCED RAMAN SCATTERING

The Gradient Field Raman effect (GFR)

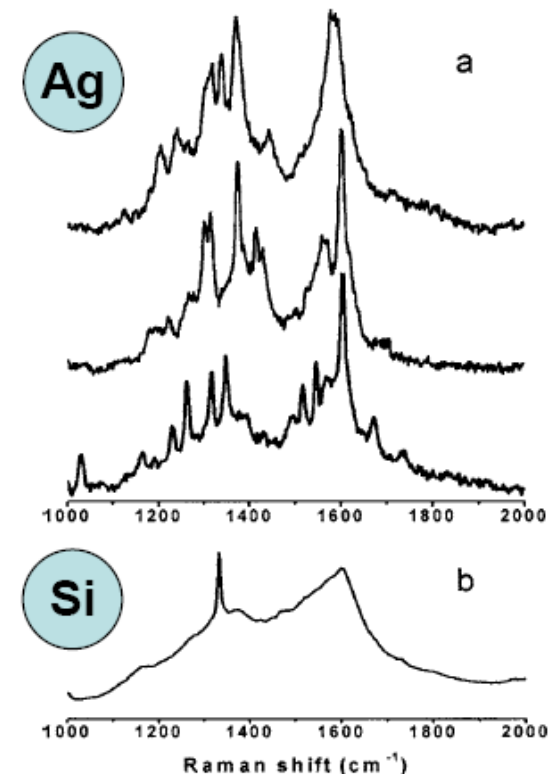
In regular Raman, the Electric field can be assumed to be constant
 $\Delta E^{\text{field}} = \text{scale of } \lambda (\sim 500\text{nm}) \gg \Delta d (\text{chemical bond}) \sim 1\text{\AA}$

In SERS, $\Delta E^{\text{field}} = \text{nanoscale}$
 \Rightarrow not negligible any more

GFR = coupling of ΔE^{field} with the bonds in vibration

\Rightarrow The selection rules are completely different:
Both Raman and IR modes can be activated
New peaks often appear in the Raman spectrum

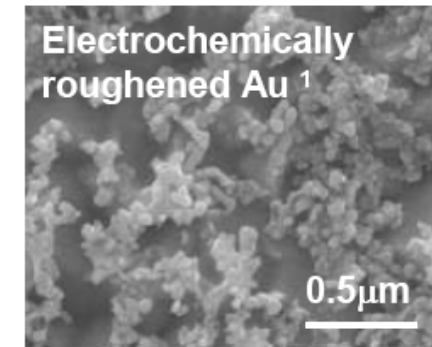
Nanodiamond ($\lambda=532\text{nm}$)



SURFACE ENHANCED RAMAN SCATTERING

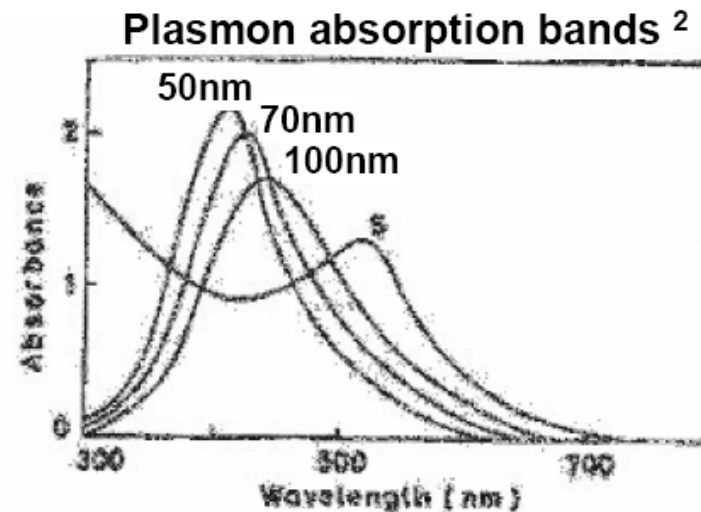
The EM enhancement is the direct consequence of the metal roughness that can be obtained by:

- oxido-reduction cycles on electrode surfaces
- metal particles vapor deposition onto a substrate
- metal particles assemblies produced via lithography
- metal colloids



The parameters that control the enhancement factor are:

- the particles size
- their shape
- their fractality
- the nature of the metal
(usually Gold, Silver, Copper)



1 Wang C. et al. Electrochem. comm. 7, 1199 (2005)

2 Mandal M. et al. Current Sci. 86, 4 (2004)

SURFACE ENHANCED RAMAN SCATTERING

2- The chemical enhancement mechanism

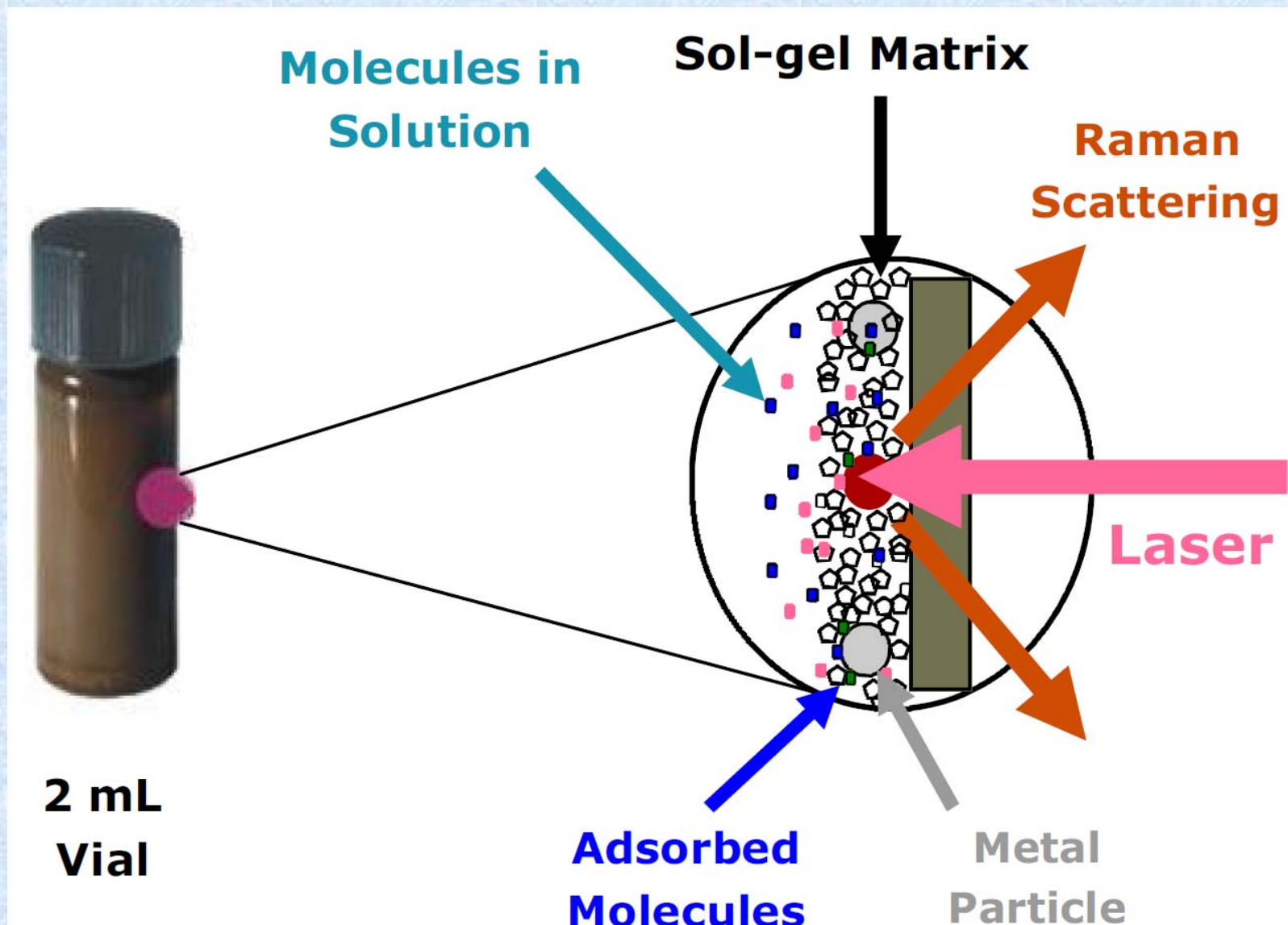
The metal-molecule proximity allow pathways of electronic coupling from which novel charge transfer intermediates emerge.

New electronic levels are created, potentially allowing for Resonant Raman

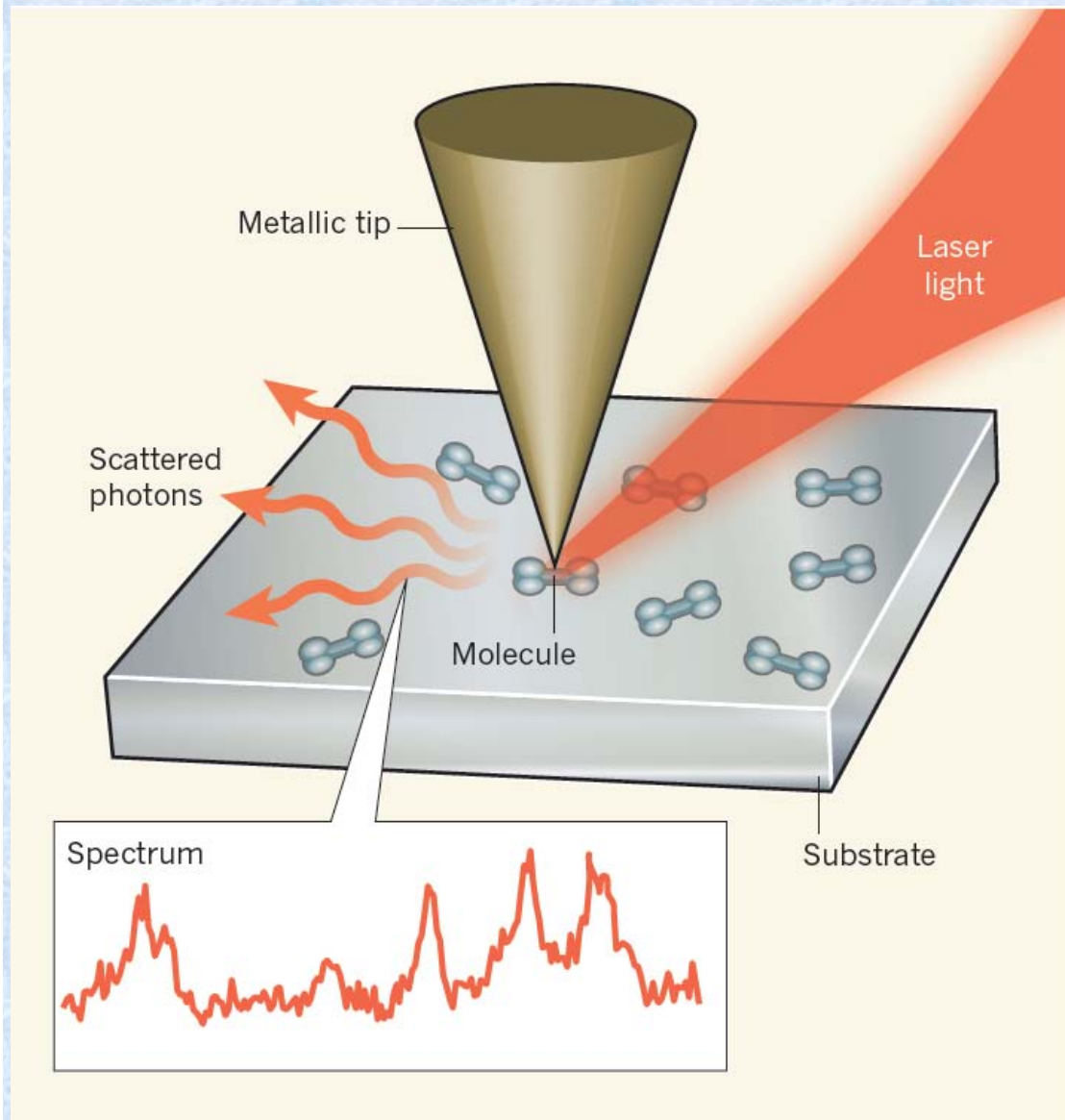
EM enhancement = change in the intensity of molecules which are scattering
Chem. Enhancement = change in the scattering cross-section (RR effect).

Chemical enhancement requires metal-molecule
electrostatic attraction or **covalent bonding**

SURFACE ENHANCED RAMAN SCATTERING

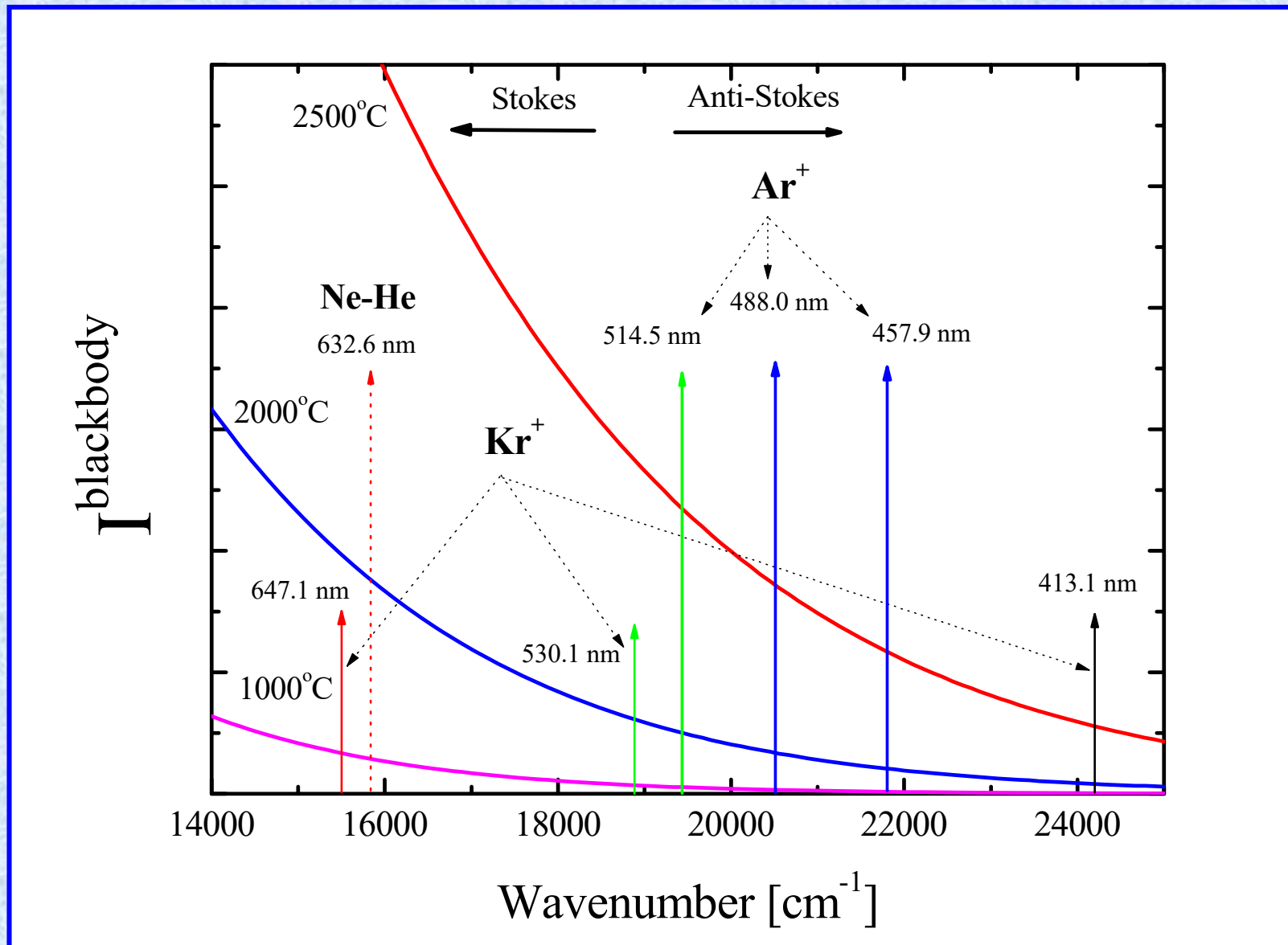


TIP ENHANCED RAMAN SCATTERING (TERS)

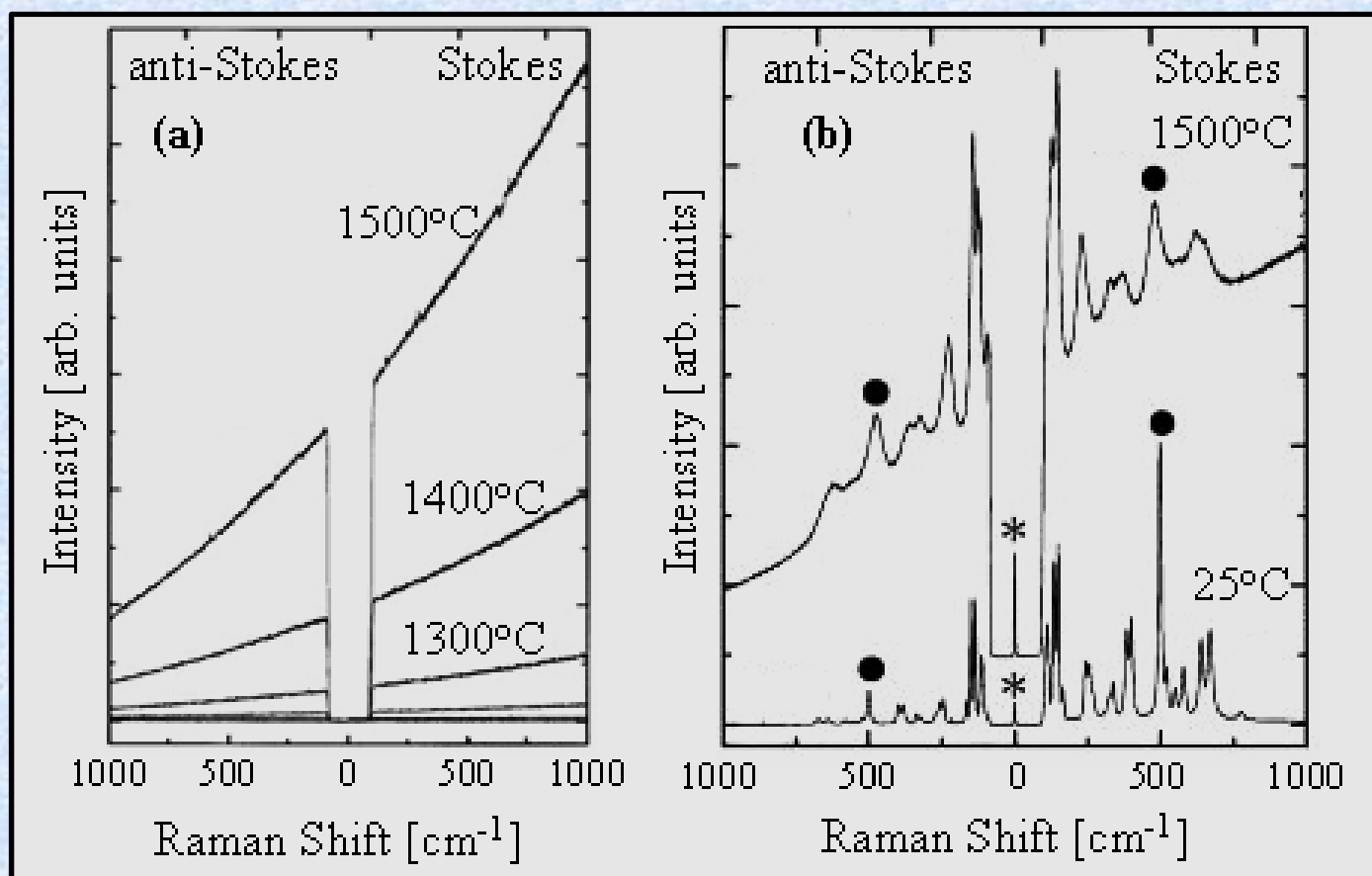


- A metallic tip that has a very sharp apex (a few nanometers across) is in close proximity to the molecule.
- The electric current arising from electrons tunneling between the tip and the sample is monitored. Laser light is then focused on the apex.
- Detection of the resulting tip-scattered photons provides a vibrational spectroscopic signature of the molecular structure.

HIGH TEMPERATURE MEASUREMENTS



HIGH TEMPERATURE MEASUREMENTS



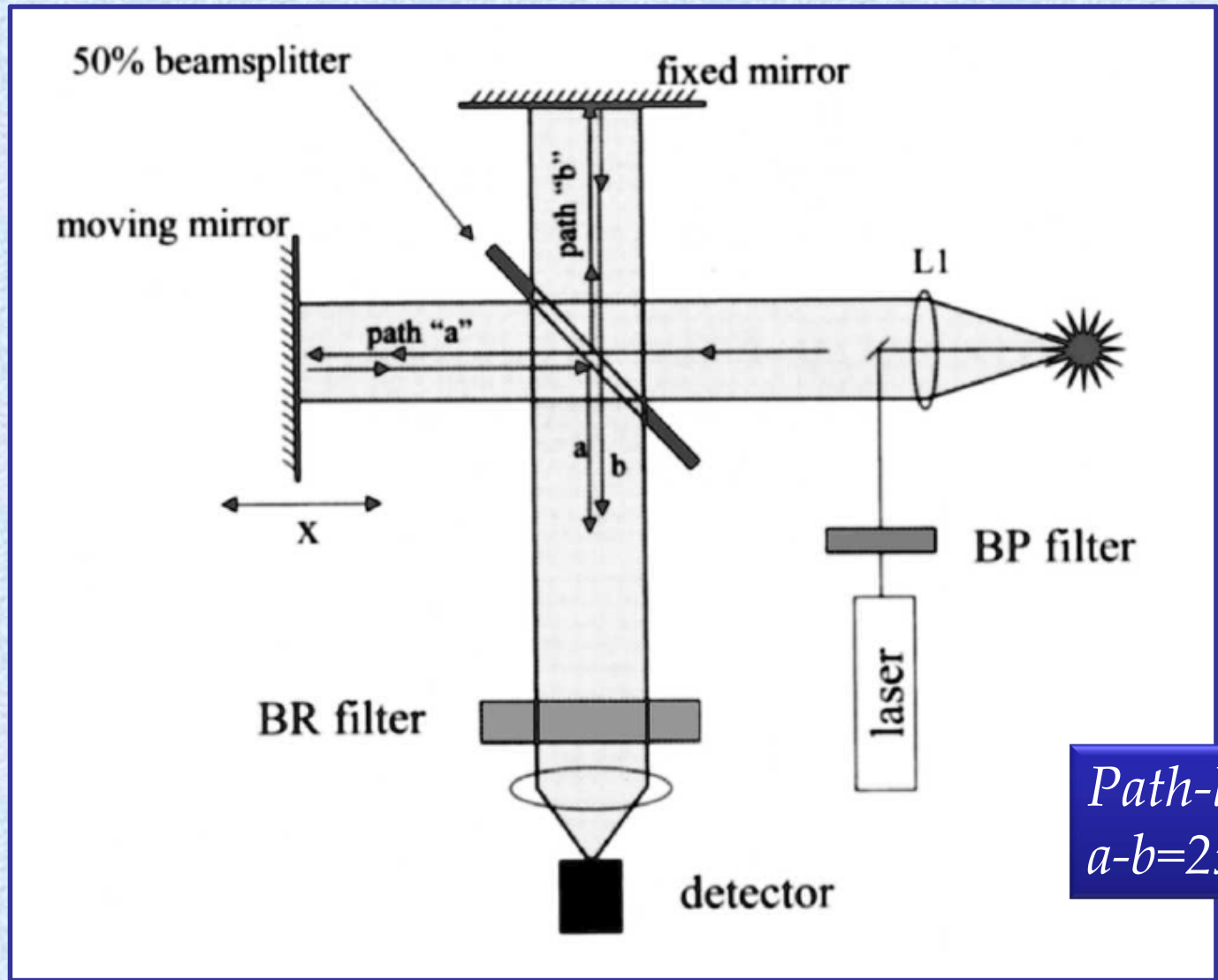
(a) Thermal emission in Stokes and anti-Stokes side for several temperatures.

(b) Stokes and anti-Stokes side Raman spectra of HfO₂ at 20 °C and 1500 °C.

Fujimori et al. *Appl. Phys. Lett.*, **79**, 937939 (2001).

NONDISPERSIVE RAMAN SPECTROMETERS

FOURIER-TRANSFORM PRINCIPLE



Wavelength
analyzer



Michelson
interferometer

Path-length difference
 $a-b=2x$

FOURIER-TRANSFORM PRINCIPLE

With motion of the moving mirror, the two beams undergo **constructive** and **destructive** interference, so that the detector signal will be **maximum** when

$$2x = m\lambda \quad (m \text{ is an integer})$$

and a **minimum** when

$$2x = (m + 1/2) \lambda.$$

For a **single input wavelength**, the detector output is a sine wave of the form:

$$\text{signal}(x) = A \cos \frac{(4\pi x)}{\lambda} = A \cos(4\pi x \bar{\nu})$$

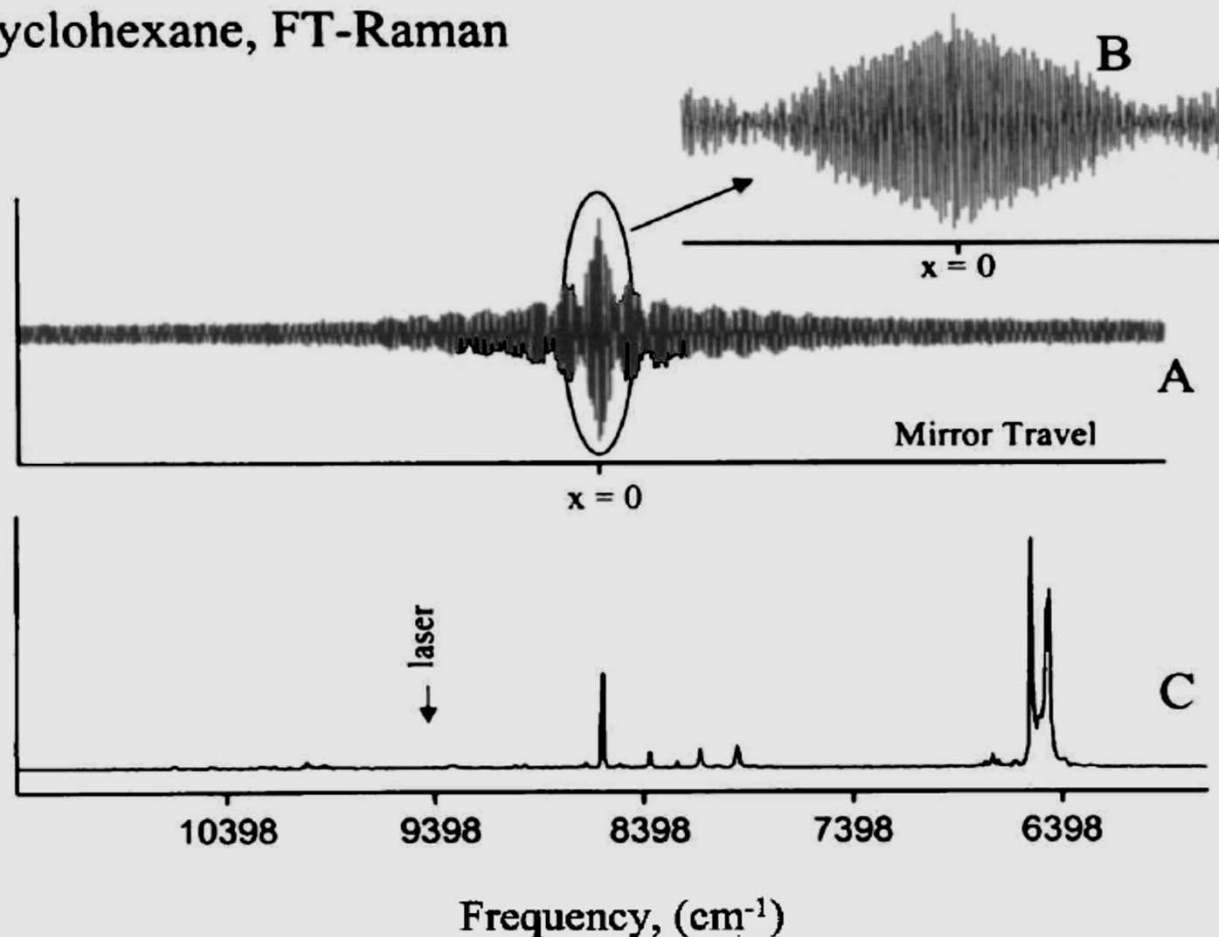
Assuming the mirror velocity is constant, equal to Γ (centimeters per second), then $x = \Gamma t$, and

$$\text{Signal}(t) = A \cos(4\pi \Gamma \bar{\nu} t)$$

FOURIER-TRANSFORM PRINCIPLE

When **many wavelengths** are present in the input spectrum, the interferogram is a sum of many sine waves of different frequency and phases.

cyclohexane, FT-Raman



The *center-burst* at $x = 0$ corresponds to zero path length difference, where all wavelengths constructively interfere.

FOURIER-TRANSFORM PRINCIPLE

Scattered light contains many wavelengths. The scattered intensity has the form:

$$I(s) = 2 \int_0^{\infty} I(v) (1 + \cos 2\pi v s) dv = 2 \int_0^{\infty} I(v) dv + 2 \int_0^{\infty} I(v) \cos 2\pi v s dv =$$

$$I_{\infty} + 2 \int_0^{\infty} I(v) \cos 2\pi v s dv$$

There is a **constant** and a **changing** part

The changing part is responsible for the interferogram generation and is called Interferometer Function

Path length
difference

$$I(v) = \int_{-\infty}^{\infty} F(s) \cos 2\pi v s ds = 2 \int_0^{\infty} F(s) \cos 2\pi v s ds$$

Fourier Transform

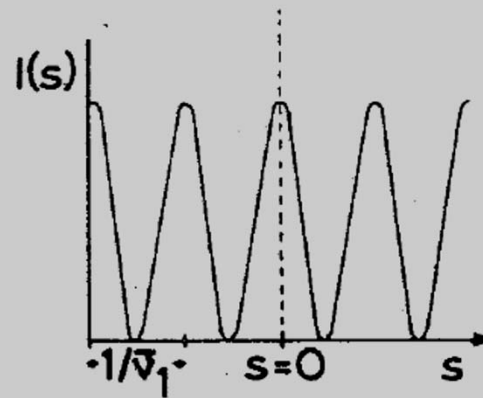
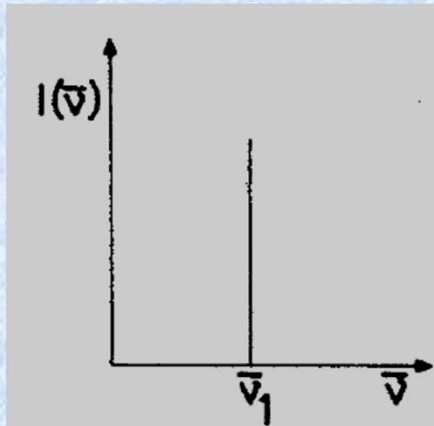


$$F(s) = 2 \int_0^{\infty} I(v) \cos 2\pi v s dv = \int_{-\infty}^{\infty} I(v) \cos 2\pi v s dv$$

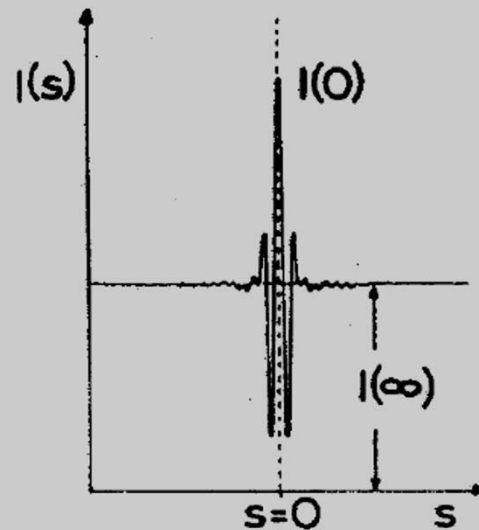
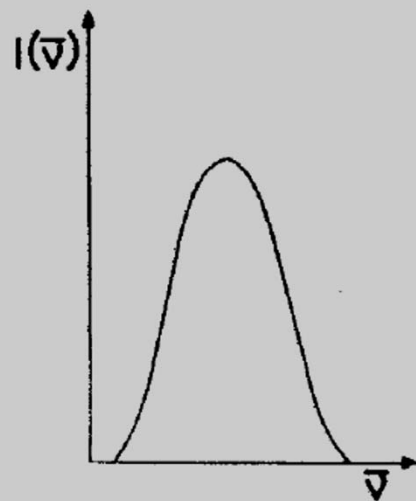
FOURIER-TRANSFORM PRINCIPLE

Spectrum

Interferogram



Monochromatic light



Polychromatic light

FOURIER-TRANSFORM PRINCIPLE

Relationship between mirror travel and resolution

$$\delta\bar{\nu} = 1/(\Delta x_{\max})$$

For example, 0.1 cm^{-1} resolution is attainable with 10 cm of mirror travel

